Influence of chars from hydrothermal carbonization and pyrolysis on carbon and nitrogen-dynamics in agricultural soils

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ABSTRACT

Leaching of nutrients from agricultural soils causes major environmental problems as well as nitrogen (N) loss as ammonia from agricultural systems is one of the major sources of atmospheric pollutants and is responsible for more than 50% of global ammonia emissions. Moreover, intensive land use and current agricultural practices have led to the degradation of soil and to decreasing content of soil organic matter (SOM). Therefore, the application of char to soil offers an option to sequester atmospheric carbon (C) and to improve soils' fertility as well as mitigate NH_3 emissions. Different types of char are used for this study as soil amendments, produced with two different processes: pyrochar produced with pyrolysis and hydrochar produced with hydrothermal carbonization. The objectives of this study were to i) determine the nutrient sorption potential of nine different char–soil mixtures in laboratory batch experiments (Article 1). Furthermore, ii) the estimation of aging-effects of chars on nutrient sorption potential in a 19-month field experiment (Article 1). In addition, iii) the effect of an admixture of pyrochar and hydrochar produced from the same substrate (*Miscanthus*) to different manure types i.e. cattle slurry and poultry litter on NH_3 emissions was investigated (Article 2), and lastly, iv) the stability against mineralization of two char types under field conditions was tested (Article 3).

Therfore, the nutrient retention capacity of pyrochars and hydrochars from three different feedstocks (digestates, *Miscanthus*, woodchips) mixed into different soil substrates (sandy loam and silty loam) was investigated with a batch-sorption experiment. Moreover, the influence of char degradation on its nutrient retention capacity was tested using the first 7 month of a 19 month *in-situ* field incubation of pyrochar and hydrochar mixed into soil at three different field sites (Article 1). During the 19 month experimental period, the ^{13}C abundance allowed the calculations of char-derived C in the soil at three sampling dates (Article 3). In a lab-incubation experiment the effect of both chars produced from biomass of *Miscanthus* mixed with manure (poultry litter and cattle slurry) on ammonia volatilization was assessed. Treatments with and without acidification were conducted to shift the ammonia/ammonium-equilibrium towards ammonium. Thus, a distinguishing between an additional pH-effect induced by chars or from ammonium adsorption was possible (Article 2).

Pyrochars showed the highest ability to retain nitrate, ammonium and phosphate, with pyrochar from woodchips being particularly efficient in nitrate adsorption. Ammonium adsorption of pyrochars was controlled by the soil type of the soil–char mixture. Some ammonium retention on sandy soils was found, but no pyrochar effect or even ammonium leaching from the loamy soil. The phosphate retention capacity of pyrochars strongly depended on the pyrochar feedstock with large phosphate leaching from digestate-derived pyrochar and some adsorption capacity from woodchip-derived pyrochar. Application of hydrochars to agricultural soils caused small, and often not

significant, effects on nutrient retention. In contrast, some hydrochars did increase the leaching of nutrients compared to the non-amended control soil. A surprisingly rapid loss of the chars' adsorption capacity after field application of the chars was found. For all sites and for hydrochar and pyrochar, the adsorption capacity was reduced by 60–80% to less or no nitrate and ammonium adsorption. While C derived from pyrochar did not change over time, hydrochar-C decreased 75±20% after 19 months *in-situ* field incubation. There was no difference in the decomposition dynamics of the chars among the three field sites with different soil types. Moreover, we did not observe a decline in decomposition rates with time but the data were well fitted with a linear one-pool decay model. The model derived mean residence times were 5±1 years for hydrochar and with larger uncertainty for pyrochar: 42±10 years. Ammonia volatilization was higher in poultry litter than in cattle slurry treatments. Pyrochars slightly increased ammonia emissions from both manures due to their alkaline pH. In contrast, hydrochars decreased the pH and consequently slightly reduced the ammonia emissions. No ammonium adsorption effects were found due to char additions.

IN CONCLUSION, neither hydrochar (slow release fertilizer or acidification medium to reduce NH_3 emissions) nor pyrochar (C-sequester) showed a multi-beneficial usage. Without additional, synergetic benefits of char applications to agricultural soils char application will not be adopted by farmers because they are expensive. The results cast doubt on the efficiency of char applications to temperate zone soils to minimize nutrient losses via leaching. Furthermore, the efficiency of char additions to reduce nitrogen losses as ammonia from manures is minor in comparison to manure acidification. Thus, while pyrochar has a high potential for C-sequestration, faster mineralization of hydrochar compared to pyrochar showed their potential to also act as a long-term fertilizer through slow nutrient release to soils.

KEYWORDS: Biochar, soil amendment, nutrient retention, C-sueqestration, ammonia volatilization

ZUSAMMENFASSUNG

Die Auswaschung von Nährstoffen aus landwirtschaftlich genutzten Böden sowie die Ammoniakverflüchtigung aus landwirtschaftlichen Systemen verursachen die größten Probleme in der Landwirtschaft. Hinsichtlich der Stickstoffverluste beträgt der Anteil der Landwirtschaft an den globalen Ammoniakemissionen 50%. Außerdem haben eine intensive Landnutzung und die derzeitige landwirtschaftliche Praxis dazu geführt, dass Böden degradieren und ihr Gehalt an organischer Bodensubstanz gesunken ist. Das Einarbeiten von Pflanzenkohle in Böden ermöglicht es, diesen Prozessen entgegenzuwirken und zusätzlich atmosphärischen Kohlenstoff zu speichern, die Bodenfruchbarkeit zu verbessern und zudem Ammoniakemissionen zu reduzieren. Zwei Arten von Pflanzenkohle aus unterschiedlichen Herstellungsprozessen standen dieser Arbeit als Bodenverbesserer zur Verfügung: die mit der Pyrolyse hergestellte Pyrokohle und die aus der Hydrothermalen Carbonisierung entstandene Hydrokohle. Die Ziele dieser Arbeit waren es i) das Nährstoffsorptionspotential von neun verschiedenen Kohle-Bodenmischungen in einem Sorptionsversuch zu untersuchen (Artikel 1). Des Weiteren wurde abgeschätzt, ii) wie sich das Sorptionspotential durch eine 19-monatige Kohle-Alterung in einem Freilandversuch verändert (Artikel 1). iii) Die Wirkung auf Ammoniakemissionen durch Hinzugabe von Pyrokohlen oder Hydrokohlen zu Rindergülle und Hühnertrockenkot wurde in einem weiteren Experiment untersucht (Artikel 2). Schlußendlich galt es unter Freilandbedingungen zu untersuchen, wie stabil beide Kohlearten gegen Mineralisation sind (Artikel 3).

Dazu wurden in einem Sorptionsversuch die Nährstoffretentionskapazitäten von Pyrokohlen und Hydrokohlen untersucht, die aus drei verschiedenen Ausgangsmaterialien (Gärreste, *Miscanthus* und Holzhackschnitzel) hergestellt und mit zwei unterschiedlichen Bodensubstraten (sandiger Lehm, schluffiger Lehm) gemischt wurden. Um die Veränderung der Nährstoffretention durch eine Kohlealterung zu überprüfen, wurde ein Sorptionsversuch mit den genutzten Pflanzenkohlen aus einem Freilandversuch durchgeführt. Die Pflanzenkohlen wurden mit dem Boden von drei verschiedenen landwirtschaftlichen Ackerflächen gemischt und jeweils vor Ort ausgebracht (Artikel 1). Der Versuch umfasste einen Zeitraum von 19 Monaten, wovon der Kohlealterungsversuch die ersten sieben Monate einnahm. Zudem wurde an zusäztlichen Probenahmezeitpunkten während der gesamten 19 monatigen Versuchsdauer die ^{13}C-Abundanz an Bodenproben bestimmt, die eine Unterscheidung des kohlebürtigen Kohlenstoffs vom bodenbürtigen Kohlenstoff ermöglicht. Zudem wurde so die Mineralisierung des kohlebürtigen Kohlenstoffs quantifiziert. In einem Laborincubationsexperiment wurde der Pflanzenkohleeinfluss auf Ammoniakemissionen von aus *Miscanthus* hergestellten Kohlen, die mit Wirtschaftsdüngern (Rindergülle, Hühnertrockenkot) gemischt wurden, untersucht. Varianten mit und ohne Ansäuerung wurden dazu verwendet, das Ammoniak/Ammoniumgleichgewicht in Richtung Ammonium zu verschieben, damit eine

Unterscheidung zwischen einem kohleinduziertem pH-Effekt von einer Ammoniumadsorption an Kohlen möglich war (Artikel 2). Pyrokohlen wiesen die höchste Retention für Nitrat, Ammonium und Phosphat auf, wobei die Pyrokohlen aus Holzhackschnitzeln am effektivsten für die Nitratadsorption waren. (Die Ammoniumadsorption der Pyrokohlen wurde beeinflusst durch den verwendeten Bodentyp der Kohle-Bodenmischungen.)

Während im sandigen Substrat Ammonium von Pyrokohlen adsorbiert wurde, konnte dies im lehmigen Substrat kaum oder gar nicht nachgewiesen werden. Das verwendete Ausgangsmaterial zur Pyrokohleherstellung war bestimmend für die Phosphatretention: die stärkste Phosphatauswassung wurde bei der Pyrokohle aus Gärresten gefunden, wobei die Pyrokohle aus Holzhackschnitzeln nur eine geringe adsorption hatte. Hydrokohlen hatten meist keinen signifikanten Einfluss auf die Nährstoffretention in den zwei untersuchten Böden. Stattdessen wiesen einige eine Erhöhung der Nährstoffauswaschung im Vergleich zu den nicht-behandelten Kontrollvarianten auf. Während des Freilandversuchs verloren die Pflanzenkohlen sehr schnell ihre Adsorptionskapazität. An allen Standorten verloren sowohl die Hydrokohle als auch die Pyrokohle bis zu 60-80% ihrer urpsrünglichen Ammonium- und Nitratadsorptionskapazität. Während der pyrokohlenbürtige Kohlenstoff sich über die 19 monatige Versuchsdauer kaum verändert hat, sank der hydrokohlenbürtige Kohlenstoff auf 75±20% des urpsrünglich eingebrachten Kohlenstoffs. Ein Unterschied in der Mineralisationsdynamik zwischen den drei Versuchsflächen konnte nicht festgestellt werden. Die Mineralisationsdaten wurden mit einen 'one-pool-decay' Modell modelliert. Dabei ergab sich für die Hydrokohle eine mittlere Verweilzeit von 5±1 Jahren und für die Pyrokohlen 42±10. Allerdings sind die errechneten Verweilzeiten für die Pyrokohlen mit einer großen Unsicherheit behaftet. Bezüglich der Ammoniakverflüchtigung war zu beobachten, dass beim Hühnertrockenkot größer als bei der Rindergülle. Die Hinzugabe von Pyrokohle erhöhte die Ammoniakemissionen leicht durch ihren alkalischen pH. Im Gegensatz dazu verminderten die Hydrokohlen durch ihren sauren pH leicht die Ammoniakemissionen. Eine Ammoniumadsorption der Kohlen konnte nicht nachgewiesen werden.

SCHLUSSFOLGERND kann gesagt werden, dass sowohl Hydrokohlen (Langzeitdünger oder Ansäuerungsmedium zur Ammoniakemissionsreduzierung) als auch Pyrokohlen (Kohlenstoffspeicher) nur jeweils einen Nutzen aufwiesen. Ohne einen Zusatznutzen werden vor allem Landwirte Pyrokohlen oder Hydrokohlen nicht als Bodenverbesserer verwenden, da sie zu hohe Anschaffungskosten haben. Die Ergebnisse lassen an einer Effizienz von Pflanzenkohleeinarbeitung in Böden zur Reduzierung der Nährstoffauswaschung aus Böden der Temperaten Zone zweifeln. Außerdem ist ihre Wirkung zur Reduzierung von Ammoniakemissionen aus Wirtschaftsdüngern sehr gering im Vergleich zu einer direkten Ansäuerung der Dünger mit Säure. Daher eignen sich Pyrokohlen lediglich zur Kohlenstoffspeicherung in Böden, wohingegen

die schnelle Mineralisierung von Hydrokohlen und die Auswaschung von Nährstoffen aus der Kohlenmatrix auf eine potentielle Nutzung als Langzeitdünger schließen lassen.

SCHLÜSSELWORTE: Biokohle, Bodenverbesserer, Nährstoffauswaschung, Kohlenstoffspeicherer, Ammoniakverflüchtigung.

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LIST OF CHEMICAL ABBREVIATIONS

Al	Aluminum
C	Carbon
^{13}C	Stable isotope ^{13}C
$\delta^{13}C$	Isotopic ratio of the stable isotopes $^{13}C/^{12}C$ between a sample and a standard.
Ca	Calcium
$CaCl_2$	Calcium chloride
CH_4	Methane
CO	Carbon oxide
CO_2	Carbon dioxide
CO_2-eq	Carbon dioxide - equivalent
Fe	Iron
H_2	Hydrogen
H_2O	Water
H_2SO_4	Disulfuric acid
H_3PO_4	Orthophosphoric acid
HCl	Hydrochloric acid
K	Potassium
Mg	Magnesium
Na	Sodium
N	Nitrogen
N_t	Total nitrogen
N_{min}	Mineral nitrogen
N_2O	Nitrous oxide
NH_3	Ammonia
NH_4^+	Ammonium
NO_3^-	Nitrate
O	Oxygen
P	Phosphor
PO_4^{3-}	Phosphate
S	Sulfur
SO_4^{2-}	Sulfite
Zn	Zinc

ABBREVIATIONS OF WORDS

AEC	Anion exchange capacity
AIC	Akaike's information criterion
ANOVA	Analysis of variance
aq	Aqueous solution
a.s.l.	Above sea level
BET-surface area	Brunauer, Emett and Teller-surface area
CEC	Cation exchange capacity
CS	Cattle slurry
DI-water	Deionized-water
DOC	Dissolved organic carbon
dw	Dry weight
EDA	π–electron donor–acceptor
fw	Fresh weight
GAM	Generalized additive models
HTC	Hydrothermal carbonization
IC	Ion chromatography
ICP-OES	Inductively coupled plasma optical emission spectrometry
IRMS	Isotope-ratio mass spectrometry
MFE	Mineral fertilizer equivalent
MRT	Mean residence time
OM	Organic matter
PAH	Polycyclic Aromatic Hydrocarbons
PL	Poultry litter
PyOM	Pyrogenic organic matter
PyC	Pyrogenic carbon
SD	Standard deviation
SE	Standard eroor
SOC	Soil organic carbon
SOM	Soil organic matter
SSA	Specific surface area
VTC	Vapothermal carbonization

SI UNITS

a	Year
cm	Centimeter
d	Day
g	Gram
g	Gravity
h	Hour
ha	Hectare
kg	Kilogram
kJ	Kilojoule
L	Liter
M	Molar concentration,1000 mol L^{-1}
MPa	Megapascal
Mg	Megagram
mg	Milligram
min	Minute
N	Equivalent concentration or normality
m	Meter
mm	Millimeter
µm	Micrometer
mL	Millliliter
Pg	Petagram
rpm	Rounds per minute

CHAPTER 1 GENERAL INTRODUCTION

Concerning the carbon-cycle, intensive land use, land use change, and current agricultural practices have exacerbated the degradation of soil including decreasing content of soil organic matter (SOM) (Lal and Bruce, 1999; Lal and Kimble, 1997; Paustian *et al.*, 1997). To counteract the increased accumulation of C in the atmosphere as CO_2 as well as to counteract soil C loss, long term carbon sequestration in agricultural soils is scheduled under article 3.4 in the Kyoto Protocol (Freibauer *et al.*, 2004; UNFCCC, 1998). Most agriculturally used soils lost 30 to 40% of their native soil organic carbon (SOC) which will further intensify by soil degradation and desertification (Don *et al.*, 2011; Poeplau *et al.*, 2011). Nevertheless, the annual increase in atmospheric CO_2 was estimated to 3.3 Pg C a^{-1} (Lal, 2004). With regard to capturing atmospheric CO_2, the global potential for C-sequestration in soils is estimated to 0.6 to 1.2 Pg C a^{-1} (Olivier *et al.*, 2013; Lal, 2003). Since the past decades, the long term storage of atmospheric C in the soil to mitigate global warming has gained increasing attention. Recommended technologies such as mulch farming, conservation tillage or no till farming, cover crops, crop rotation, nutrient management with compost or precision farming (Smith, 2004; Shaver *et al.*, 2002; Gregorich *et al.*, 2001; Fullen, 1998; Singh *et al.*, 1998; Uhlen and Tveitnes, 1995; Woodbury and Breslin, 1992) reduce the rate of CO_2 fluxes from soil to the atmosphere but, however, are rather insufficient.

Furthermore, regarding to the nutrient-cycle, excessive application of mineral fertilizer or manures such as cattle slurry or poultry litter to agricultural soils is one of the major drivers for various threats to the environment (Laird *et al.*, 2010; Beusen *et al.*, 2008; Liang *et al.*, 2006). Loss of nutrients (e.g. ammonium (NH_4^+), nitrate (NO_3^-), phosphate (PO_4^{3-})) from fertilizer may induce soil acidification, indirect and direct greenhouse gas emissions, as well as eutrophication of the receiving water-bodies (Karaca *et al.*, 2004). Additionally, agricultural systems are among the major sources of atmospheric pollutants, such as ammonia (NH_3). They are responsible for more than 90% of total NH_3 emissions in Europe (Erisman *et al.*, 2008) and over 50% of the global NH_3 emissions (Bouwman *et al.*, 1997). Atmospheric deposition of nitrogen (N) can destabilize natural and semi-natural terrestrial ecosystems, where biomass growth is often N limited and native species are adapted to low N availability. In Europe, the reduction of NH_3 emissions has been becoming of increasing relevance for more than a decade. In the 'Thematic Strategy on Air Pollution' (CEC, 2005), the European Comission aimed at reducing around 30% of agricultural NH_3 emissions in the EU25 until 2020 compared to 2000. Manure acidification (Kai *et al.*, 2008) and adjusted manure application methods (Webb *et al.*, 2010; Flessa and Beese, 2000) are proposed as promising options to decrease NH_3-volatilization, retain nutrients and prevent leaching but have reached their technological limitations or are restricted in some states.

Therefore, new technologies are required to i) increase the capture-rates of atmospheric C to soils and store it stabilized as SOC; ii) To decrease NH_3-volatilization from organic manure applied to soils and retain nutrient leaching from soil into subsequent water bodies and enhance nutrient use efficiency with the aim to reduce the amount of needed fertilizer. In the past years, amendment of soil and/or manures with char gained increasing attention and may be an option to counteract negative impacts to the environment.

1.1 Definitions

Different specifications and definitions in char are common depending on the use and/or genesis of char: Char is termed ‘pyrogenic organic matter’ (PyOM) or ‘pyrogenic carbon’ (PyC) when parts of plant biomass was converted into char by incomplete combustion due to wildfires initiated by anthropogenic or native causes at the place where they grow (Velasco-Molina *et al.,* 2016; Santín *et al.,* 2015a; Santín *et al.,* 2015b; Knicker, 2007). Otherwise, when char is only used as C-storage medium (e.g. as energy-carrier) than the solid product is termed 'charcoal' (Maddox, 2013). Furthermore, char is termed 'biochar' when the solid product is derived from a variety of organic feedstocks such as sewage sludge, digestates, woods, and other forestry or agricultural residues (Hale *et al.,* 2013; Yao *et al.,* 2012; Lehmann and Joseph, 2009) and, in addition, three requirements are fulfilled (Schimmelpfennig and Glaser, 2012; Lehmann and Joseph, 2009):

i) the char was produced by pyrolysis,
ii) the char is used as soil conditioner and to sequester atmospheric C in soils, and
iii) the char is stable against degradation and/or mineralization for in minimum 2000 years.

However, this implicates the current discrepancy in definition: When chars with the aim to fulfill the three requirements described above are gained from 'newer' non-pyrolysis production processes (e.g. hydrothermal carbonization (HTC) (Libra *et al.,* 2011; Yu *et al.,* 2004) or vapothermal carbonization (VTC) (Funke *et al.,* 2013)), than they cannot termed as ‘biochar’.

In this doctoral thesis, the definition by genesis will be uses to explicitly distinguish between both production processes and its resulting chars with their different properties and characteristics:

- the char is gained from pyrolysis = pyrochar
- the char is gained from HTC = hydrochar

In this doctoral thesis, when refers to both char types, then the term 'char' will be used.

CHAPTER 2 CARBONIZATION PROCESSES AND TECHNOLOGIES

The carbonization processes of biochar, charcoal and other carbonaceous materials are generally dominated by a wide temperature range (350 to 1200°C) under oxygen limited conditions that inhibit a complete combustion of the origin feedstock. Charcoal is produced in brick-kilns or pits, e.g., for heating, cooking or in the metallurgy industry, whereas biochar was converted from biomass residues especially as soil amendment (Joseph *et al.*, 2009; Lehmann and Joseph, 2009). The used technique, production temperature, time, feedstock moisture, wood species and size strongly influence the yield and quality of the charcoal (Schenkel *et al.*, 1998). With regard to the current environmental restrictions and discussions about large amounts of greenhouse gas emissions, revised technologies were used at present. For the traditional production process, Pennise *et al.* (2001) estimated that on average 0.77 to 1.63 kg CO_2-eq were emitted per kg charcoal. Modern technologies for e.g. charcoal or biochar production offer the opportunity to produce carbonized materials under defined conditions (e.g. carbonization time and temperature) and to use other types of biomasses in addition to wood as feedstock. At present, two main groups of production processes are established: i) the thermo-chemical conversion of organic feedstock materials via pyrolysis and gasification and ii) hydrothermal techniques such as hydrothermal carbonization (liquid water) and vaporization (water vapor).

Regarding to the basic compounds of the biomass feedstock (cellulose, hemi-cellulose, lignin), either thermo-chemical as well as hydrothermal conversion techniques generate a chemical transformation by reducing the water and/or oxygen content of the feedstock resulting in an increase in the carbon concentration (e.g. carbonization, dehydration, depolymerization, dehydrogenation, decarboxylation, recondensation), which determines the product yield, stability against degradation and the amount of functional groups on chars' surface (Schimmelpfennig and Glaser, 2012; Keiluweit *et al.*, 2010; Titirici and Antonietti, 2010; Knicker, 2007).

2.1 Pyrolysis and its resulting char type

In the following, only the production processes for the char types used in this doctoral thesis will be described. The pyrolysis process is characterized by a wide range of temperatures with limited oxygen supply that inhibit complete combustion of the used feedstock (Karaosmanoğlu *et al.*, 2000). The conditions for pyrolysis can be distinguished between:

i) process duration (slow (hours to days), intermediate (10-30 sec) and fast (~1 sec) pyrolysis) (Bridgwater 2012), as well as

ii) process temperature (high (>800°C), medium (500-800°C), and low (<500°C) temperature pyrolysis (Lehmann and Joseph, 2009).

However, Antal and Grønli (2003) suggested an additional differentiation with regard to the resulting C-content as function of the process temperature of chars:

i) High C-containing chars: 850-500°C process temperature and a C-content of around 80-99% (mostly from wood as feedstock).

ii) Medium C-containing chars: 850-330°C process temperature and a C-content of around 80-60% (mostly from digestates, manures or grasses as feedstock).

iii) Low C-containing chars: 850-250°C process temperature and a C-content of around 60-20% (mostly from poultry litter or nutshells as feedstock).

Furthermore, pyrolysis is an exothermic process, so once it is started no external energy is needed to preserve the process. A modern pyrolysis furnace is the PYREG-reactor: The feedstock enters through a dosing system and is heated up. As there is little or no oxygen present in the reactor, the feedstock is not burned, but carbonized (PYREG, 2013). In the carbonization process syngas is formed, which is burned completely in a combustion chamber, so that there are very low exhaust emissions (PYREG, 2013). The components of the biomass that is used as a feedstock for carbonization can behave differently in the process of carbonization: Cellulose, hemicellulose and lignin are the major components of plants. The decomposition of these components in the process of pyrolysis is temperature dependent. Hemicellulose and Cellulose decompose relatively quickly when heated, while lignin decomposes in a very slow process. Besides these three, plant material also contains other organic compounds like resins, fats, phenolics and phytosterols, but these do not have a significant influence on the char yield in pyrolysis (Lehmann and Joseph, 2009). Anyhow, this doctoral thesis refers to the term 'pyrochar' for the solid product resulting from this production process. On average, pyrolysis yields (depending on feedstock) consists of about (on dry wood basis) 12-35% solid char products as well as 30-75% liquid (bio-oil), and 13-35% gaseous (CO_2, CO, CH_4, H_2) byproducts (Bridgwater, 2012; Spokas *et al.*, 2009).

2.2 Hydrothermal Carbonization and its resulting char type

Hydrothermal carbonization (HTC) for the production of 'hydrochars' includes the heating of biomass with addition of water and a catalyst (e.g. citric acid) at temperatures between 180 and 250°C under autogenous pressure up to 2-2.5 MPa for several hours (Wiedner *et al.*, 2013; Hoekman *et al.*, 2011; Libra *et al.*, 2011; Funke and Ziegler, 2010; Yu *et al.*, 2004 ; Bergius, 1913). The advantage of HTC compared to pyrolysis is the potential carbonization of wet feedstocks containing 50 to 80% water (e.g. municipal solid waste, animal manures, or sewage sludge) without energy-intensive pre-drying before the process (Libra *et al.*, 2011). Therefore, the energy consumption and costs are less in the HTC process than pyrolysis. The HTC process offers higher yield compared to pyrolysis but also a higher amount of dissolved organic compounds and lower amounts of gases (Cao *et al.*, 2011; Libra *et al.*, 2011). Like pyrolysis, HTC is an exothermic process that needs no external energy once it is activated (Titirici *et al.*, 2007). This provides hydrochars and pyrochars as a useful material for various purposes and applications such as fuel or source material for C-rich 'nano'-materials as well as soil amendment (Kang *et al.*, 2012; Qian *et al.*, 2006).

2.3 Properties of pyrochar and hydrochar

The chemical and physical properties of charcoals or pyrochars differ significantly to hydrochars (less aromatic and less condensed), through different thermochemical reactions and carbonization processes (Yao *et al.*, 2012; Cao *et al.*, 2011). Furthermore, also different feedstocks and production conditions for either hydrochar or pyrochar can vary widely in their physical and chemical properties such as pH and these in turn are still reflected in the physic-chemical properties of the resulting chars (Eibisch *et al.*, 2013; Cantrell *et al.*, 2012). These properties partly explain the chars' effects and behavior in and on soil. The most important properties are the chars' elemental composition, the black carbon content, its surface area and the contained amount of polyaromatic hydrocarbons.

2.3.1 Molar H:C and O:C-ratio

The elemental composition and the black carbon content of a char indicate the degree of carbonization and recalcitrance against mineralization in the soil. Schimmelpfennig and Glaser (2012) examined these properties for chars produced with different methods and feedstocks. They found that chars produced by the HTC process had a significantly higher molar H:C ratio than chars produced in a wood gasifier, in a 'Pyreg' reactor, in a charcoal stack in a rotary kiln or by other processes (Figure 2.1).

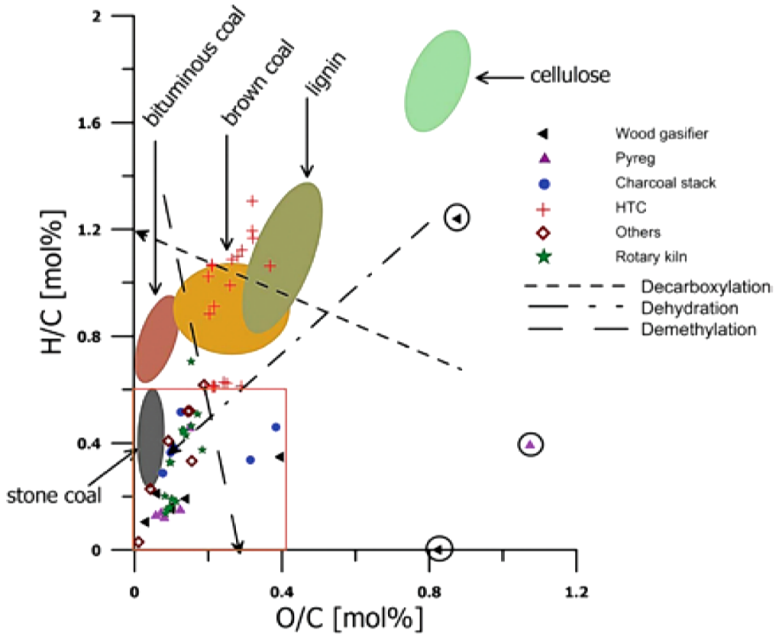

Figure 2.1 Van Krevelen diagram displaying the atomic ratios of different chars, compared with various organic materials (Schimmelpfennig and Glaser, 2012:6).

A high molar O:C ratio indicates that a high amount of polar functional groups are bound to the char. These groups can attract water by electrostatic interactions. If many functional groups are bound to the char, this prevents the materials structure to be densely packed. As a consequence these chars have a higher chemical reactivity and a lower stability in soils than chars with a lower molar O:C ratio. These atomic ratios of the hydrochars are comparable to those of brown-coal, with

a relatively high molar H:C ratio pointing to a low grade of demethylation and decarboxylation. Other chars have more chemical similarity to stone-coal, with a low molar H:C ratio indicating high aromaticity and molecular homogeneity (Schimmelpfennig and Glaser, 2012). Furthermore, hydrochars have higher H:C and O:C ratios which mean that they have higher amounts of plant-derived surface functional groups on chars' surface (Schimmelpfennig and Glaser, 2012). In general, both hydrochar and pyrochar differ significantly in their pH-value. The acid pH-value of hydrochars is dominated by acidic functional groups on chars' surface (Eibisch *et al.*, 2013; Kastner *et al.*, 2009). Due to its high ash-content and without any preparatory treatment (e.g. washing), the pH-value of pyrochars is mainly alkaline (Lehmann and Joseph, 2009). With regard to the specific use of chars, there is a competition between the stability and functionality of chars. The more stable the chars are, the lower is their functionality due to decreasing functional groups on chars' surface (Schimmelpfennig and Glaser, 2012).

2.3.2 Specific Surface Area

The specific surface area (SSA) of a char is an indicator for its porosity. If the char is applied to soil, its surface area can have influence on the soils ecology and its water balance. The major part of the surface area is made up by micropores, which are smaller than 2 nm in size (Lehmann and Joseph, 2009). These pores are created during the production process by the loss of volatile elements such as CO_2, H_2O, and CO. The micropores can hold water by capillary forces, so that the biochar functions like a sponge: It takes up water in wet conditions and releases it in dry conditions, contributing to a better water availability in the soil (Schimmelpfennig and Glaser, 2012; Lehmann and Joseph, 2009). It has been shown that the BET-surface area of a biochar is influenced by the production process and in specific by the highest carbonization temperature during this process. There is a positive relationship between production temperature and BET-surface area, up to a temperature of around 750°C. This can be explained by changes in the chemical structure of the feedstock: Aromatic C-structures are generated at high temperatures and provide a matrix in which micropores can form (Lehmann and Joseph, 2009). In line with these findings, Schimmelpfennig and Glaser (2012) found that the BET-surface area of hyrdrochar (which are produced at temperatures of only ~200°C) are significantly lower than the BET-surface area of other chars which are produced at higher temperatures. The surface area of hydrochars is around 8 m^2/g, while other chars exhibit a surface area of up to 300 $m^2\ g^{-1}$ (Schimmelpfennig and Glaser, 2012). Eibisch *et al.* (2013) found that the surface area of hydrochars correlated positively with the mineralization of the chars' C when incubated with soil.

2.3.3 Black Carbon Content

For the purpose of C sequestration it is desirable to produce chars with a high content of black carbon, because this is a very stable form of organic matter. Schimmelpfennig and Glaser (2012) found that the black carbon content of hydrochars lies around 5%, while that of biochars produced

in a Pyreg-reactor ranges from 10 to 15%. Chars produced in a charcoal stack exhibit the highest black carbon content of up to 35%. Thus, the black carbon content seems to be depending on the production process, but could also be influenced by the feedstock.

Content of Polyaromatic Hydrocarbons

The amount of polyaromatic hydrocarbons (PAHs) that a char contains can be used as an indicator for its toxicity. PAHs in chars can be formed during the production process because the feedstock's chemical structure is broken down by the high temperature (Lehmann and Joseph, 2009). Both hydrochar and pyrochars contains very low PAH contents, whereas biochars from a wood gasifier can contain more than 4000 mg PAH kg^{-1} (Schimmelpfennig and Glaser, 2012).

CHAPTER 3 STATE-OF-THE-ART AND GAPS OF KNOWLEDGE

3.1 Chars for nutrient management in agricultural soils and the influence of char aging

Both pyrochars and hydrochars contain nutrients which can be released slowly into the rhizosphere (Eibisch *et al.,* 2013; Spokas *et al.,* 2011; Taghizadeh-Toosi *et al.,* 2011), but more important is the pyrochars' ability to adsorb nutrients due to its high surface charge density and CEC. The leaching and adsorption of NO_3^-, NH_4^+, and PO_4^{3-} to various activated C and charcoals has been studied (Ding *et al.,* 2010; Bandosz and Petit, 2009b). However, studies concerning the sorption behavior of pyrochar, and especially hydrochars, are rare. Previous studies focusing on soil–char mixtures have shown that leaching of NO_3^-, NH_4^+, and PO_4^{3-} from soils amended with pyrochar or hydrochar was frequently reduced due to adsorption on the respective char (Bargmann *et al.,* 2014b; Sarkhot *et al.,* 2012; Ding *et al.,* 2010; Laird *et al.,* 2010). Other nutrients which are not particularly prone to leaching, such as PO_4^{3-}, have also been reported to be retained by application of pyrochar (Xu *et al.,* 2014b; Morales *et al.,* 2013; Laird *et al.,* 2010). In summary, these studies imply a strong variation in leaching or retention behavior of chars, which seems to depend on feedstock and production process.

However, benefits have been tested mostly for pyrochar amended tropical soils with few comparative studies for temperate soils or hydrochars. This is one of the main reasons why neither pyrochar nor hydrochar application is considered in agricultural practice in the temperate zone at the moment. Even though chars, especially pyrochars, are relatively stable in soils, an increasing number of studies have suggested that biotic and abiotic processes can lead to degradation of char and thus change its surface properties and sorption behavior (Liu *et al.,* 2013; Hale *et al.,* 2011; Steinbeiss *et al.,* 2009; Cheng *et al.,* 2008). The physical structure and chemical properties of hydrochars result in a lower recalcitrance towards microbial degradation compared to pyrochars (Bargmann *et al.,* 2014a; Hale *et al.,* 2011; Steinbeiss *et al.,* 2009). Furthermore, hydrochars release a higher amount of dissolved organic carbon (DOC) which might be easily mineralized. Hence, soil amended with hydrochars increases microbial-biomass production and immobilization of mineral nitrogen (Bargmann *et al.,* 2014a; Lehmann *et al.,* 2011), and an increased nitrification from NH_4^+ to NO_3^- may occur. Over time, slow char aging due to oxidation may lead to carboxylic and phenolic functional groups on the chars' surface and thus negative charges. On the other hand, the atomic C content and positive surface charge on the edge sites of aromatic compounds will be reduced (Cheng *et al.,* 2008; Glaser *et al.,* 2000). Furthermore, surface oxidation increases CEC per unit C and the charge density (Liang *et al.,* 2006), but a higher anion exchange capacity (AEC) has been found for aged pyrochars as well (Mukherjee *et al.,* 2011). At the same time, pyrochars may adsorb organic matter (OM), which blocks char surfaces and reduces their sorption capacity (Mukherjee *et al.,* 2011). However, so far these long-term changes in char properties and

consecutive functions have been ignored in most char studies on nutrient retention, which may lead to systematic bias.

IN SUMMARY, according to the majority of studies (Xu *et al.*, 2014a; Hale *et al.*, 2013; Morales *et al.*, 2013; Knowles *et al.*, 2011; Lehmann *et al.*, 2003), char may be a potential melioration for soils by decreasing nutrient leaching via improved adsorption properties. However, there is only little knowledge on the nutrient sorption potential of pyrochars compared to hydrochars, and the influence of aging/degradation on nutrient sorption. The influence of char properties resulting from different carbonization methods and different feedstock materials on nutrient sorption potential is also insufficiently understood. Furthermore, no systematic comparison of different feedstock materials on nutrient sorption has yet been conducted, and the effect of aging of chars on their sorption potential has not yet been investigated.

3.2 Chars for managing ammonia emissions from organic manures

The fate of N in soils following the application and decomposition of a variety of materials with high N content such as manure or the organic residuals of household waste (Sánchez-Monedero *et al.*, 2001; Eklind and Kirchmann, 2000;), sewage sludge (Malińska *et al.*, 2014; Sánchez-Monedero *et al.*, 2001) or poultry litter (Steiner *et al.*, 2010) has been widely studied. However, only a few studies investigated the effects of char amendment to reduce NH_3 emissions from manure. When ammonium (NH_4^+), urea or uric acid is adsorbed to chars, lower amounts of reactive N can be volatized as NH_3. Spokas *et al.* (2011) showed that chars mixed with slurry can inhibit NH_3 volatilization by surface interactions with NH_4^+ and NO_3^-.

Chars can influence NH_3 emissions either by changing the pH since NH_3 volatilization is pH sensitive or by adsorbing NH_4^+ as precursor of NH_3. NH_3 can also be adsorbed onto the char in the presence of acidic functional groups on the chars' surface or if the char has an acidic pH (Kastner *et al.*, 2009). The study of the adsorption capacity of NO_3^- and NH_4^+ to various activated C and chars showed adsorption onto pyrochars and slight or no adsorption on hydrochars (Ding *et al.*, 2010; Bandosz and Petit, 2009a).

IN SUMMARY, studies concerning the effect of pyrochar, and especially hydrochar, on soils and manure NH_3 emissions in the temperate zone are rare, and the interaction of different char- manure mixtures is still not understood. Furthermore, no comparison study of the two different char types (pyrochar vs. hydrochar) on reducing NH_3 emissions has been conducted yet. Moreover, most studies were conducted without soil. Thus, the effect of char addition to different types of manure via changes in pH or ammonium adsorption remains unclear.

3.3 Chars for atmospheric C-sequestration in agricultural soils

Climatic conditions, water content, soil type, the initial SOM content of the soil and the nutrient availability is determined for soil microbial activity and thus C mineralization (Lu *et al.*, 2014; Zimmerman *et al.*, 2011). Abiotic and biotic processes can degrade chars and subsequently modify its properties e.g. sorption behavior (Liu *et al.*, 2013; Hale *et al.*, 2011; Steinbeiss *et al.*, 2009; Cheng *et al.*, 2008). Abiotic processes in soils affect mainly the labile C fraction decomposition rate as well as the short-term char oxidization indicated by a decrease in pH, as well as an increase in cation exchange capacity (CEC) and oxygen (O) content (Cheng *et al.*, 2006). Cheng *et al.* (2006) suggested that the formation of carboxylic functional groups is the reason for enhanced CEC during oxidation. For effective soil amendment, char degradation is more relevant than C sequestration because nutrients that are incorporated into chars can be released (Abiven *et al.*, 2011). Over time, slow char aging due to oxidization may produce carboxylic and phenolic functional groups. On the other hand, the atomic C content and surface positive charge on the edge sites of aromatic compounds will be reduced (Cheng *et al.*, 2008; Cheng *et al.*, 2006; Glaser *et al.*, 2000).

Generally, laboratory incubation studies were used to assess the C-mineralization dynamics of char amended soils and first long term experiments in the laboratory reported both: A high recalcitrance against mineralization of pyrochar and a low recalcitrance of hydrochar (Bamminger *et al.*, 2014; Kuzyakov *et al.*, 2014; Lu *et al.*, 2014; Gajić *et al.*, 2012). All studies agree that chars can be mineralized, but the rates are different depending on environmental conditions and the quality of the char (Zhao *et al.*, 2015).

TO SUMMARIZE, most studies examining the stability of char are too short in order to deduce data on mid and long-term char stability and are conducted as incubation studies in the laboratory were environmental controlling factors on char stability are ignored. No systematic comparison about the recalcitrance of pyrochars compared to hydrochars from the same feedstock in a long term field experiment has been conducted yet. Most studies, however, are still conducted in a laboratory setting with often unknown bias in results and limited transferability into the ‘real world’. Furthermore, there is a large discrepancy between decomposition rates and mean residence times estimated from incubation studies showing slower char-C mineralization and life-times of millennia (Bamminger *et al.*, 2014; Fang *et al.*, 2014; Kuzyakov *et al.*, 2014; Gajić *et al.*, 2012) versus field experiments showing shorter times of decades to centuries (Malghani *et al.*, 2014; Jones *et al.*, 2012).

CHAPTER 4 MAIN OBJECTIVES

An essential understanding of fundamental properties and their consequences for the application to the environment, especially to the 'critical zone' soils is crucial for future strategies in soil amendment with chars for C-sequestration or nutrient retention. In this dissertation, pyrochar and hydrochar derived from different feedstock materials (digestates, *Miscanthus*, woodchips) are investigated in order to establish their suitability as soil amendment for long-term C sequestration and increase of soil fertility. Furthermore, N-management in agriculture gets raising importance. For this, the influence of char application to organic manures was tested to assess if chars has a reducing effect on NH_3 volatilization.

Effects of fresh and aged chars from pyrolysis and hydrothermal carbonization on nutrient sorption in agricultural soils (Chapter 6)

The objectives of this study are to:

1. Determine the nutrient sorption potential of nine different char–soil mixtures in laboratory batch experiments. The hypotheses are:

   Regarding their specific surface area (Eibisch *et al.,* 2013; Lehmann and Joseph, 2009):

   H_1: The adsorption potential on nutrients is higher for pyrochar than for hydrochar.

   With regard to the different contents of lignin and/or cellulose of char-feedstock and resulting chemo-physically properties after carbonization (SSA, surface functional groups) (Eibisch *et al.,* 2013; Schimmelpfennig and Glaser, 2012):

   H_2: The adsorption potential on nutrients for both chars decreases in the following order: Woodchips > *Miscanthus* > digestates.

   The influence of different soil types on the potential sorption capacity of chars are in competition with soils' pH, CEC, AEC, SSA, organic matter content, and texture (Alling *et al.,* 2014; Hale *et al.,* 2011). Therefore the hypothesis is:

   H_3: The adsorption potential of both chars is more inhibited by silty loam than by sandy loam.

2. Assessing the effect of aged *vs*. fresh chars (pyrochar and hydrochar from *Miscanthus*) on nutrient sorption potential in a field experiment. It is hypothesized that degraded chars have a higher content of surface functional groups which could adsorb more nutrients than fresh chars (Hale *et al.,* 2011; Steinbeiss *et al.,* 2009). For this the hypothesis is:

   H_4: The adsorption potential of both chars are higher for aged chars than fresh chars.

Mitigation of ammonia emissions from manures: Acidification is more effective than char application (Chapter 7)

The objective of this study is to investigate the effect of an admixture of pyrochar and hydrochar produced from the same substrate (*Miscanthus*) to different manure types i.e. cattle slurry and poultry litter on NH_3 emissions.

Regarding the physico-chemical properties (pH, SSA) of chars on adsorption potential it is hypothesized that:

H_5: The adsorption of NH_4^+ will reduce NH_3 volatilization more strongly than the char-induced pH-effect.

H_6: The reduction of NH_3 volatilization is higher for pyrochar compared to hydrochar treatments.

Stability of pyrochar and hydrochar in different agricultural soils - a new field incubation method (Chapter 8)

In order to evaluate chars' potential as agricultural amendment and the option to mitigate climate change, it is necessary to know its stability against mineralization once they are applied to soils. Hence, the aim of this study was to assess the stability of two char types under field conditions.

Referring to the stability of chars it is hypothesized that:

H_7: Hydrochar are less stable than pyrochar.

Table 5.1 Overview for the used materials and methods of each experiment.

Study	Objective	Lab or field	Char	Soil/Sites	Methods	Main-analyzes regarding the objectives	Equipment
Batch-equilibrium experiments (Chapter 6)	i) Sorption potential of chars on anions/kations ii) Sorption potential of aged chars on anions/kations	i) Lab ii) Field	***Lab:*** Hydrochars and pyrochars from the conversion of woodchips, *Miscanthus*, and digestates. ***Field:*** Hydrochar and pyrochar from *Miscanthus*	***Lab:*** Haplic Luvisol & haplic Cambisol ***Field:*** 3 agricultural field sites in Nothern Germany: -Bortfeld (Siltic Cambisol) -Querenhorst (Arenic Planosol) -Volkmarsdorf (Cambic Planosol)	***Lab:*** Batch-sorption procedures after OECD (2000) ***Field:*** See char-stability experiment; Batch-sorption procedures after OECD (2000)	1. Determine zinc to calculate the dilution correction factor (inert tracer). 2. Determine the residual NO_3^-, NH_4^+, PO_4^{3-} in the batch solutions to calculate the amount of adsorbed or leached nutrients	1. Extraction via microwave aqua regia digestion and determined using ICP-OES. 2. IC for anions and ICP-OES for cations
NH_3 volatilization experiment (Chapter 7)	Assesing which char-factor has more influence on NH_3 volatilization from manures: pH or adsorption.	i) Lab incubation study ii) Lab adsorption study	Hydrochar and pyrochar from *Miscanthus*	***i) Lab incubation study:*** Ap horizon of a Cambic Planosol ***ii) Lab adsorption study:*** no soil used	***i) Lab incubation study:*** a volatilization-diffusion experimental setup with forced-draft system to determine NH_3 emissions from poulty litter and/or cattle slurry treated with chars. ***ii) Lab adsorption study:*** Batch-adsorption experiment	***i) Lab incubation study:*** NH_3 was trapped in gas-wash-flask filled with H_3PO_4. NH_3 was chemically converted into NH_4^+ which was analyzed. ***ii) Lab adsorption study:*** Determine the residual NH_4^+ in the batch medium (poultry litter or cattle slurry) to calculate the amount of adsorbed NH_4^+.	***i) Lab incubation study & ii) Lab adsorption study:*** NH_4^+ from the gas-wask-flask and the adsorption experiment was analyzed using photometric continuous flow analyzer (SKALAR)
Char stability experiment (Chapter 8)	Hydrochar and pyrochar stability against mineralization	Field study	Hydrochar and pyrochar from *Miscanthus*	3 agricultural field sites in Nothern Germany: -Bortfeld (Siltic Cambisol) -Querenhorst (Arenic Planosol) -Volkmarsdorf (Cambic Planosol)	-Mini-plots in a randomized split-plot design with 3 replicates per char and control treatment per site. -Sampling: right after application (T0), after 7 month (T1) and finally after 19 month (T2) by taking five soil cores with a split-tube sampler from each mini-plot.	1. Determining zinc to calculate the dilution correction factor (inert tracer). 2. C and N at soil and soil-char samples to calculate SOC for bulk soil. 3. δ13C at soil and soil-char samples to determine the proportion of char derived C.	1. Extraction via microwave *aqua regia* digestion and determined using ICP-OES. 2. Dry combustion. 3. Stable isotope ratio mass spectrometry (IRMS) coupled to an elemental analyzer.

5.1 Materials

5.1.1 Chars

Chars for the laboratory batch experiments

The nine chars that were used for laboratory batch experiments originated from the same setup as the chars used in Eibisch *et al.* (2013). These chars were derived from HTC and pyrolysis and were produced from three feedstock materials with different physicochemical properties (woodchips (95% poplar, 5% willow), *Miscanthus x giganteus*, and digestates (99% maize)). We used these feedstocks to test different common renewable biomasses differing in their cellulose and lignin content. The hydrochars were carbonized with water (1:10, w/w) in a batch reactor for 6 h with a pressure of 2 MPa at 200 (hereafter referred to as Hydro200 in Chapter 6) and 250°C (hereafter referred to as Hydro250 in Chapter 6; SmartCarbon AG, Jettingen, Germany). Pyrochars were produced in a Pyreg reactor (PYREG GmbH, Dörth) for 0.75 h at 750°C (designated hereafter as Pyro750 in Chapter 6). In order to simulate field aging, we compared unwashed chars with washed chars in the laboratory experiment. Washing was assumed to be capable of simulating aging of the char as initially bound nutrients or salts would be removed. Washing was carried out by shaking 4.5 g of biochar with 1 L of deionized water in an overhead shaker at 9 rpm for 4 h and thereafter the solution was filtered with pleated paper filter (grade: 3 hw; diameter: 150 mm; 65 g m^2) and filtrate (pyrochar or hydrochar) was dried for 24 h at 105°C. Washing effects were only studied in the pyrochar and hydrochar applied to silty loam mixtures, because highest nutrient leaching or adsorption effects were expected for this soil.

Chars for the field experiment and NH_3 volatilization experiment

The feedstock for both, hydrochar and pyrochar was above ground biomass of the C_4-plant *Miscanthus x giganteus*. Pyrochar was carbonized in a Pyreg reactor (PYREG GmbH, Dörth) at 750° for C 0.75 h. Hydrochar was produced with water (1:10, w/w) in a tabular reactor (3 m^3) at 200°C and 2 MPa for 11 h by AddLogicLabs / SmartCarbon (Jettingen, Germany). To catalyze the dehydration process in order to increase the C content in the solid product, citric acid powder was added to the *Miscanthus* (0.03 kg citric acid / 1 kg *Miscanthus*) (Wang *et al.*, 2010). Both chars were dried at 40°C and sieved through 2 mm.

5.1.2 Soils & experimental sites

Soils for the laboratory batch-experiments

Two soils were used for the char–soil mixtures: a silt loam (Blagodatskaya *et al.*, 2014) from a cropland site at the Thünen Institute in Braunschweig, Germany (52°17' N, 10°26' E; 80 m a.s.l.), and a sandy loam from a cropland site of the University of Göttingen (Reinshof), Germany (51°28' N, 9°58' E; 205 m a.s.l.). The soil was dried at 105°C to inhibit any microbial activity and sieved <2 mm.

Soils and sites for the field experiment (char aging and stability)

For the investigation of the effect of aging of the chars in the field, chars were incubated in situ at three cropland sites in the North German lowland (mean annual temperature 8.8°C, around 600 mm precipitation). The three sites differ mainly in their soil texture and are located in Bortfeld (sandy loam (SL); 52°28' N, 10°41' E; 80 m a.s.l.), Volkmarsdorf (sandy loam (SL); 52°36' N, 10°89' E; 105 m a.s.l.), and Querenhorst (loamy sand (LS); 52°33' N, 10°96' E; 112 m a.s.l.). All sites were managed according to common regional practice with conventional tillage and fertilizing. Crop rotations were barley (2012), winter wheat (cover crop), and sugar beet (2013) (Querenhorst); barley (2012), mustard (cover crop), and sugar beet (2013) (Volkmarsdorf); and potatoes (2012) and sugar beet (2013) (Bortfeld).

Soils for the NH_3 volatilization experiment

Soil was sampled from the Ap-horizon (0-30 cm) of a Cambic Planosol at a cropland site in the North German lowland in December 2014 (mean annual temperature 8.8°C, around 600 mm precipitation, 52°36'N, 10°89'E, 105 m a.s.l.). The site was managed according to common regional practice with conventional tillage and fertilization. Crop rotation was barley (*Hordeum vulgare*) (2012), mustard (*Sinapis arvensis*) (cover crop), sugar beet (*Beta vulgaris* ssp. *vulgaris*) (2013), followed by winter wheat (*Triticum aestivum*) (2014). After sampling, the soil was sieved to ≤4 mm and stored for 4 weeks at 4°C until use in the experiment.

5.1.3 Manures for the NH_3 volatilization experiment

Cattle slurry (CS) and poultry litter (PL) were used as manure amendments. Four subsamples of 6 L CS were collected and each was mixed to obtain a representative slurry sample. For CS, pH was measured undiluted. CS was stored close in a cold storage room at 4°C. Four 1 kg subsamples of PL were sampled from one manure pit and were mixed afterwards to receive a representative PL sample. PL was also stored close in a cold storage room at 4°C. Sub treatments were established with an addition of acid to the char/manure mixtures in order to differentiate an induced adsorption process of chars from a pH-effect through char addition on NH_3 volatilization. In these treatments,

one part of the manures was acidified with sulfuric acid (H_2SO_4) to achieve a pH between 5.5 and 5.8. To avoid a destruction of organic compounds in the manures, 98% sulfuric acid was diluted with DI-water. With regard to the dry matter content of CS, we added a 25% H_2SO_4 to CS (0.02 mL acid: 1 g fw CS). To improve the mixing process of chars and PL, we added DI-water 1:1 (fw/g water) to the mixture. Regarding to the dry matter contents of PL, we added 12.5% H_2SO_4 to PL (0.25 mL acid : 1 g fw PL : 0.75 mL H_2O).

5.2 Methods

5.2.1 Laboratory aging of chars (Chapter 6)

In order to simulate field aging, we compared unwashed chars with washed chars in the laboratory experiment. Washing was assumed to be capable of simulating aging of the char as initially bound nutrients or salts would be removed. Washing was carried out by shaking 4.5 g of biochar with 1 L of deionized water in an overhead shaker at 9 rpm for 4 h and thereafter the solution was filtered with pleated paper filter (grade: 3 hw; diameter: 150 mm; 65 g m^2) and filtrate (pyrochar or hydrochar) was dried for 24 h at 105°C. Washing effects were only studied in the pyrochar and hydrochar applied to silty loam mixtures, because highest nutrient leaching or adsorption effects were expected for this soil.

5.2.2 Field aging of chars (Chapter 6&8)

At all three sites, the two different types of chars were mixed into the soil in March 2013 in a randomized split-plot design. Mini-plots (plot size: 70 × 70 cm; plot depth: 25 cm) were triplicated and divided into three blocks for each site so that every site consists of nine mini plots: three were soil plots amended with pyrochar (soil+pyrochar+zinc), three with hydrochar (soil+hydrochar+zinc) and three plots served as control (soil+zinc). The distance between each mini-plot in one block was 200 cm. At each plot, soil was dug out and mixed with chars in a cement mixer in order to thoroughly mix the char and the soil. The char amendment was adjusted to double the soils' C-content, which corresponds to 100 Mg char ha^{-1}. Additionally, elementary zinc powder (particle size < 45 µm; Merck, Darmstadt, Germany) was added to the soil or soil-char mixtures in a concentration of 450 mg kg^{-1} soil as an inert tracer in order to increase sevenfold the natural zinc-concentration in the used soils to be able to correct for blending or attenuation with the surrounding soil e.g. due to tillage (leading to a final concentration of around 500 mg Zn kg^{-1} soil, when assuming a background concentration of about 50 mg Zn kg^{-1} soil. The mini-plots were not physically separated from the field site but mixing with the surrounding soil was possible. We marked every plot centrically by putting one metal bar (5×1 cm) below the plough-horizon to a depth of 35-40 cm to make a precise relocation easier. In addition, every plot-center was

georeferenced by GPS. The advantage of the mini plots was that the farmers could manage the field sites with the research plots in the same way similar to every other field.

5.2.3 Soil Sampling (Chapter 6&8)

Soil samples were taken in March 2013 right after mixing the soil with chars (designated as T_0). After seven month (October 2013), and after 19 month (October 2014) the second and third sampling was carried out (designated as T_1 and T_2) by taking five randomly distributed soil cores to a depth of 25 cm with a split-tube sampler (5 cm diameter) from each plot. Afterwards, samples were dried at 40°C and sieved to ≤ 2 mm and a subsample was finely ground for further analysis.

5.2.4 Laboratory batch-sorption experiments (Chapter 6)

Soil–char mixtures used solely in the laboratory were produced by mixing 0.5 g of char with 10 g of soil in order to roughly double the soil's C content. Preliminary sorption kinetic experiments were conducted to determine the sorption equilibrium by shaking the batches for 4, 8, 12, 24, and 48 h at 9 rpm in an overhead shaker. Based on the results of the kinetic experiments, shaking time for the determination of the sorption isotherms was set to 24 h. Soil–char mixtures and 10.5 g of soil only (control) were added to 40 mL of a nutrient solution in a 50 mL plastic centrifuge tube. Six concentration levels of a nutrient solution containing several nutrients that were chosen in order to mimic a "typical" agricultural soil solution were used (Table 3). In addition, the pH value of the solution was adjusted to 6 by adding HCl. Triplicates were measured for each concentration level. The pH was measured immediately after shaking in the char/soil-solution mixtures. Thereafter, suspensions were centrifuged at 4500 rpm for 30 min. The supernatant was aspirated with a syringe and filtered through 0.45 µm membrane filters (CHROMAFIL PET-45/25 disposable syringe filters, Macherey-Nagel).

5.2.5 NH_3 volatilization experiment (Chapter 7)

To determine NH_3 emissions, we used the volatilization-diffusion experimental setup with forced-draft system (Figure 5.1) similar to Roelcke *et al.* (1996) and Rachhpalsingh and Nye (1986). Humidified air (90% relative air humidity) was passed over the soil surface in the jars with an air flow of 16.3 exchange volumes min^{-1} (corresponding to a flow rate of 4.1 L min^{-1} per jar) accordance with Roelcke *et al.* (1996). The air-tight screw cap lids for every jar were designed similar to those of Pacholski *et al.* (2006). Ammonia was trapped as NH_4^+ in a subsequent gas wash flask containing 200 mL of 0.0125 *N* H_3PO_4. In a pre-study it was checked whether emitted NH_3 was completely trapped in the first wash flask. This was done by connecting a second trap to the exhaust air of the first wash flask.

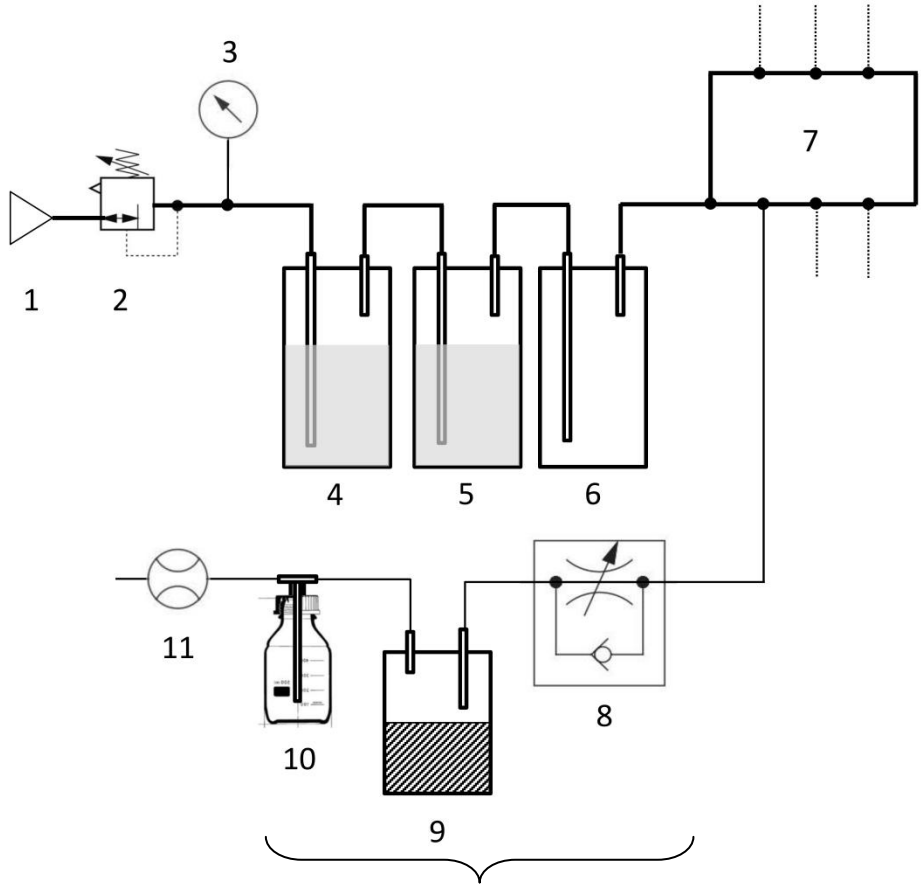

Figure 5.1 Forced-draft system extended after Roelcke *et al.* (1996) and Rachhpalsingh and Nye (1986). Numbers: 1=air compressor; 2=air pressure regulation controller; 3=manometer; 4 & 5=air humidifier filled with water; 6=air pressure compensating vessel and water trap; 7=main compressed air hose with junctions to further NH_3-units; 8=one-way-restrictor to regulate the air flow through the NH_3-unit; 9=soil column with a lid after Pacholski *et al.* (2006); 10=gas wash flask containing 200 mL of 0.0125 *N* H_3PO_4; 11=flow meter (optional, removable).

The volatilization-diffusion experimental setup was used to conduct an incubation experiment under controlled conditions in a climate chamber with 10°C air temperature during a 4-week period. Overall, a total of 26 treatments were established, each run in quadruplicate (Table 3). Additionally to the soil/char/manure/acid treatments, 250 mL blinds (empty jars) were also run in quadruplicate. The treatments without soil were carried out in order to evaluate the influence of the chars on NH_3 volatilization from the manures. Sub-treatments with acid addition to the char/manure mixtures were conducted in order to differentiate an induced adsorption process of chars from a pH-effect through char addition on NH_3 volatilization. Treatments with soil were carried out in order to quantify the effect of either pyrochar or hydrochar on NH_3 volatilization from manure applied to soil. For this purpose, we filled 978 g soil with a bulk density of 1.2 g cm^{-3} in a 1 L glass jar (resulting headspace volume was around 250 mL, soil layer thickness was 20 cm). Subsequently, manure, manure-char, and manure-char-acid mixtures were applied to the soil surface. Manures were applied using mineral fertilizer equivalents (MFE) which indicate the N-use efficiency relative to mineral fertilizer N-use efficiency (UNITO, 2014). According to the corresponding MFE, we

wanted to reach an N application rate of 60 kg N ha^{-1} corresponding to a typical N application rate in maize crops after sowing (April) until July (Wendland and Fischer, 2013; LWK-Ni, 2010) via surface application with a trailing hose for CS and even spreading for PL. Trailing hose application covering 0.12 m^2 per 1 m^2 (12%) (hose diameter / -distance = 4 cm / 30 cm) was adapted to our manure application to soil surface in the incubation jars. PL was applied punctually in the center of the soil surface with a diameter of 3 cm.

Hence, to reach the N application rate of 60 kg N ha^{-1} and with regard to the soil surface area in the jars (88.25 cm^2), we added 2.41 g (dw) CS (corresponds to 75.6 mg N; ~40% as NH_4^+-N; MFE=70% (LWK-Ni, 2013)) and 2.59 g (dw) PL (corresponds to 66.2 mg N; ~30% as NH_4^+-N; MFE=80% (LWK-Ni, 2013)) per jar, respectively. Char-CS mixtures were produced by either mixing 0.24 g of pyrochar or hydrochar with 2.41 g (dw) CS. With regard to the dry matter content of CS, we added a 25% H_2SO_4 to CS. Char-PL mixtures were produced by either mixing 0.26 g of pyrochar or hydrochar with 2.59 g (dw) PL. The added char amounts correspond to a 10% char addition to manures' dry weight. To improve the mixing process of chars and PL, we added DI-water 1:1 (fw/g water) to the mixture. Regarding to the dry matter contents of PL, we added 12.5% H_2SO_4 to PL. All mixtures were filled into the glass jars and were closed air tight. During incubation, the water content of the soil was controlled by weight and corrected when necessary: at days 3 and 5 we irrigated the surface of all treatments with 2-4 g deionized (DI)-water to compensate the water loss caused by the strong air exchange.

5.2.6 Soil mineral nitrogen

Soil mineral nitrogen (N_{min} = NO_3^--N + NH_4^+-N) was determined for pure manure and manure-soil as well for acidified and non-acidified treatments after 24 h and 7 d. An additional sample set of manure/char/acid mixtures without soil, similar to that used in the incubation experiment, was set up closed and stored airtight/unventilated for a 24 h at 10°C. Afterwards N_{min} concentrations of manures determined after a 24 h equilibrium period were used as an initial start value. After 7 d, treatments without soil from the volatilization experiment were used to determine the final N_{min} concentration at the end. All samples were extracted by shaking for 1 h to a ratio 1:20 (sample : extracting agent) with 0.01 M $CaCl_2$ to determine N_{min}. After 7 d, manure/char/acid treatments with soil were freshly homogenized. 200 g homogenized soil samples were then extracted with 600 mL 0.01 M $CaCl_2$ by shaking for 1 h.

5.3 Analyzes and measurements

5.3.1 pH-measurements of chars, manures, and soils

The pH-value of soils and chars was determined in 0.01 M $CaCl_2$ with a ratio of 1:5 (volume char/soil : volume solution). For CS, pH was measured undiluted. Before the pH measurement of PL, we diluted 5 g with 25 g deionized (DI)-water (1:5). Both manures were stirred and pH was measured after 10 min waiting time with a pH combination electrode.

5.3.2 Elemental and ionic analyzes of chars and soils

The C and N content was determined via dry combustion (TruSpec, LECO Corp., St. Joseph (MI), USA). Oxygen and hydrogen contents of chars as well as from the raw material were determined with an elemental analyzer (Vario EL3, Elementar, Hanau, Germany). Element contents of chars (e.g. P, Ca, Mg, Na, K, S) of the prepared samples were analyzed using inductively coupled plasma-optical emission spectroscopy ICP-OES (Varian Liberty 150, Agilent, Palo Alto, USA). Zinc concentrations for article 3 were extracted using microwave *aqua regia* digestion and determined using ICP-OES (Varian 725-ES, Agilent, Palo Alto, USA). For the batch-experiments, ion concentrations of the filtrates were analyzed using ion chromatography (IC) (METROHM 761) for anions (NO_3^-, PO_4^{3-}) and inductively coupled plasma chromatography (ICP) (ICS-90 Dionex/Thermo Fisher Scientific) for cations (NH_4^+). In the NH_3 volatilization experiment, samples from the gas-wash-flask and N_{min} extractions were analyzed for NH_4^+-N using a photometric continuous flow analyzer (SKALAR San++ Continuous-Flow Analyzer, Breda, The Netherlands). Total nitrogen (N_t) was measured on fresh manures using the Kjeldahl method. The NH_4^+ content was determined via distillation and titration using 10 g manure and 50 mL DI-water.

5.3.3 Delta-^{13}C signatures

The $\delta^{13}C$ signatures of the pure chars, the control soils, and soil-char mixtures were determined using stable isotope ratio mass spectrometry (IRMS) (Delta plus, Thermo Fisher Scientific, Bremen, Germany) coupled to an elemental analyzer (CE Instruments FLASH EA 1112, Thermo Fisher Scientific, Bremen, Germany).

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CHAPTER 6 EFFECTS OF FRESH AND AGED CHARS FROM PYROLYSIS AND HYDROTHERMAL CARBONIZATION ON NUTRIENT SORPTION IN AGRICULTURAL SOILS

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Abstract

Leaching of nutrients from agricultural soils causes major environmental problems that may be reduced with amendments of chars derived from pyrolysis (pyrochars) or hydrothermal carbonization (hydrochars). Chars are characterized by a high adsorption capacity – i.e. they may retain nutrients such as nitrate and ammonium. However, the physicochemical properties of the chars and hence their sorption capacity likely depend on feedstock and the production process. We investigated the nutrient retention capacity of pyrochars and hydrochars from three different feedstocks (digestates, *Miscanthus*, woodchips) mixed into different soil substrates (sandy loam and silty loam). Moreover, we investigated the influence of char degradation on its nutrient retention capacity using a 7-month in situ field incubation of pyrochar and hydrochar mixed into soils at three different field sites. Pyrochars showed the highest ability to retain nitrate, ammonium and phosphate, with pyrochar from woodchips being particularly efficient in nitrate adsorption. Ammonium adsorption of pyrochars was controlled by the soil type of the soil–char mixture. We found some ammonium retention on sandy soils, but no pyrochar effect or even ammonium leaching from the loamy soil. The phosphate retention capacity of pyrochars strongly depended on the pyrochar feedstock with large phosphate leaching from digestate-derived pyrochar and some adsorption capacity from woodchip-derived pyrochar. Application of hydrochars to agricultural soils caused small, and often not significant, effects on nutrient retention. In contrast, some hydrochars did increase the leaching of nutrients compared to the non-amended control soil. We found a surprisingly rapid loss of the chars' adsorption capacity after field application of the chars. For all sites and for hydrochar and pyrochar, the adsorption capacity was reduced by 60–80% to less or no nitrate and ammonium adsorption. Thus, our results cast doubt on the efficiency of char applications to temperate zone soils to minimize nutrient losses via leaching.

6.1 Introduction

Excessive application of mineral fertilizers to agricultural soils is one of the major drivers for various threats to the environment (Laird *et al.*, 2010; Liang *et al.*, 2006). An excess of nutrients may induce soil acidification, increase direct and indirect greenhouse gas emissions (Karaca *et al.*, 2004), and cause eutrophication of the receiving water bodies. However, mineral fertilization has also been the major driver for increased global agricultural production during the last decades. Therefore, technologies are required to both decrease nutrient leaching from soils and enhance nutrient use efficiency with the result that less fertilizer is needed. Amendment of soils with chars is proposed as one promising option to retain nutrients and prevent leaching (Lehmann and Joseph, 2009).

These chars are the solid charcoal product derived from the thermal transformation of a variety of organic feedstocks such as digestates, sewage sludge, woods, and other forestry or agricultural residues (Hale *et al.*, 2013; Yao *et al.*, 2012). At present, two main processes for the production of chars that are intended for application to soil are used: the first production process, slow pyrolysis, is the combustion and conversion of biomass at processing temperatures above 450°C under oxygen-free conditions. In the following, the solid product derived from pyrolysis will be termed pyrochar. Pyrochars are characterized by a high degree of aromaticity (Keiluweit *et al.*, 2010; Lehmann *et al.*, 2006) and recalcitrance against degradation or mineralization (Glaser *et al.*, 2002). Second, hydrothermal carbonization (HTC) is a lowtemperature production process (temperatures between 180 and 300°C) under high pressure (2–2.5MPa) with water for several hours (Funke and Ziegler, 2010; Libra *et al.*, 2011; Wiedner *et al.*, 2013). In the following, we will refer to the solid product from the HTC as hydrochar. Hydrochars have recently received increasing attention since wet feedstock can also be carbonized without drying pretreatment (Funke and Ziegler, 2010). Hydrochars are characterized by a lower degree of carbonization and thus more aliphatic (C) but smaller amounts of aromatic C and lower specific surface area (SSA) compared to pyrochars (Eibisch *et al.*, 2013; Titirici *et al.*, 2008). Besides general differences between pyrochar and hydrochar, their properties differ strongly depending on the feedstock, carbonization processes parameters, and subsequent thermochemical reactions (Eibisch *et al.*, 2015; Eibisch *et al.*, 2013; Cantrell *et al.*, 2012; Yao *et al.*, 2012; Cao *et al.*, 2011).

For the past 10 years, the application of pyrochar, and later on of hydrochar, to agricultural soils has become a center of attention as an option to store atmospheric C in soil to mitigate global warming. Additionally, a variety of positive co-benefits are attributed to pyrochar-amended soils: an increase in water retention capacity (Abel *et al.*, 2013; Glaser *et al.*, 2002); reduction of greenhouse gas emissions such as nitrous oxide (N_2O) and methane (CH_4); and an enhanced crop productivity due to the retention of plant available nutrients in the rhizosphere (Lehmann and Joseph, 2009),

increased soil pH and soil cation exchange capacity (CEC) (Liang *et al.*, 2006), and preservation of toxic compounds (Chen and Yuan, 2011).

Both pyrochars and hydrochars contain nutrients which can be released slowly into the rhizosphere (Eibisch *et al.*, 2013; Spokas *et al.*, 2011; Taghizadeh-Toosi *et al.*, 2011), but more important is the pyrochars' ability to adsorb nutrients due to its high surface charge density and CEC. The leaching and adsorption of nitrate (NO_3^-), ammonium (NH_4^+), and phosphate (PO_4^{3-}) to various activated C and charcoals has been studied (Ding *et al.*, 2010; Bandosz and Petit, 2009). However, studies concerning the sorption behavior of pyrochar, and especially hydrochars, are rare. Previous studies focusing on soil–char mixtures have shown that leaching of NO_3^-, NH_4^+, and PO_4^{3-} from soils amended with pyrochar or hydrochar was frequently reduced due to adsorption on the respective char (Bargmann *et al.*, 2014b; Sarkhot *et al.*, 2012; Ding *et al.*, 2010; Laird *et al.*, 2010). Laird *et al.* (2010) applied 20 g kg^{-1} pyrochar from hardwood to an agricultural soil, which decreased the leaching of NO_3^- from swine manure by 10 %. Yao *et al.* (2012) reported increased NO_3^- adsorption of up to 4 %, as well as leaching rates of up to 8% from aqueous solution. Other studies showed that NO_3^- (Hale *et al.*, 2013; Jones *et al.*, 2012; Castaldi *et al.*, 2011;), as well as NH_4^+ leaching, was decreased by 94% due to pyrochar application to a Ferralsol in a 37-day soil column leaching experiment (Lehmann *et al.*, 2003). Furthermore, both NH_4^+ adsorption by up to 15% from aqueous solution and leaching by up to 4% into solution were observed (Yao *et al.*, 2012). Other nutrients which are not particularly prone to leaching, such as PO_4^{3-}, have also been reported to be retained by application of pyrochar (Xu *et al.*, 2014; Morales *et al.*, 2013; Laird *et al.*, 2010). For example, Laird *et al.* (2010) reported up to 70% reduced PO_4^{3-}-P leaching in a soil column experiment mixed with 20 g kg^{-1} pyrochar. In contrast, Yao *et al.* (2012) observed up to 5% PO_4^{3-}-P leaching from aqueous solution for pyrochars from bamboo and hydrochars from peanut hull. In summary, these studies imply a strong variation in leaching or retention behavior of chars, which seems to depend on feedstock and production process.

Char application has been promised to be multi-beneficial. However, benefits have been tested mostly for pyrochar amended tropical soils with few comparative studies for temperate soils or hydrochars. This is one of the main reasons why neither pyrochar nor hydrochar application is considered in agricultural practice in the temperate zone at the moment. Even though chars, especially pyrochars, are relatively stable in soils, an increasing number of studies have suggested that biotic and abiotic processes can lead to degradation of char and thus change its surface properties and sorption behavior (Liu *et al.*, 2013; Hale *et al.*, 2011; Steinbeiss *et al.*, 2009; Cheng *et al.*, 2008). The physical structure and chemical properties of hydrochars result in a lower recalcitrance towards microbial degradation compared to pyrochars (Bargmann *et al.*, 2014a; Hale *et al.*, 2011; Steinbeiss *et al.*, 2009). Furthermore, hydrochars release a higher amount of dissolved

organic carbon (DOC) which might be easily mineralized. Hence, soil amended with hydrochars increases microbial-biomass production and immobilization of mineral nitrogen (Bargmann *et al.*, 2014a; Lehmann *et al.*, 2011), and an increased nitrification from NH_4^+ to NO_3^- may occur. Over time, slow char aging due to oxidation may lead to carboxylic and phenolic functional groups on the chars'surface and thus negative charges. On the other hand, the atomic C content and positive surface charge on the edge sites of aromatic compounds will be reduced (Cheng *et al.*, 2008; Cheng *et al.*, 2006; Glaser *et al.*, 2000). Furthermore, surface oxidation increases CEC per unit C and the charge density (Liang *et al.*, 2006), but a higher anion exchange capacity (AEC) has been found for aged pyrochars as well (Mukherjee *et al.*, 2011). At the same time, pyrochars may adsorb organic matter (OM), which blocks char surfaces and reduces their sorption capacity (Mukherjee *et al.*, 2011). However, so far these long-term changes in char properties and consecutive functions have been ignored in most char studies on nutrient retention, which may lead to systematic bias.

In summary, according to the majority of studies (Xu *et al.*, 2014; Morales *et al.*, 2013; Hale *et al.*, 2013; Knowles *et al.*, 2011; Lehmann *et al.*, 2003), char may be a potential melioration for soils by decreasing nutrient leaching via improved adsorption properties. However, there is only little knowledge on the nutrient sorption potential of pyrochars compared to hydrochars, and the influence of aging/degradation on nutrient sorption.

The influence of char properties resulting from different carbonization methods and different feedstock materials on nutrient sorption potential is also insufficiently understood. Furthermore, no systematic comparison of different feedstock materials on nutrient sorption has yet been conducted, and the effect of aging of chars on their sorption potential has not yet been investigated. The objectives of this study are to first determine the nutrient sorption potential of nine different char–soil mixtures in laboratory batch experiments and to investigate the influence of (i) char type (pyrochar vs. hydrochar), (ii) soil type (sandy loam vs. silty loam), and (iii) char feedstock (woodchips, digestate, and *Miscanthus*). Secondly, we want to assess the effect of aged vs. fresh chars (pyrochar and hydrochar from *Miscanthus*) on nutrient sorption potential in a field experiment.

6.2 Materials and methods

6.2.1 Production and general properties of pyrochars and hydrochars and their corresponding feedstocks

The nine chars that were used for laboratory batch experiments originated from the same setup as the chars described in Eibisch *et al.* (2013, 2015). These chars were derived from HTC and pyrolysis and were produced from three feedstock materials with different physicochemical properties (digestates (99% maize), woodchips (95% poplar, 5% willow), and *Miscanthus*). The

hydrochars were carbonized with water (1:10, w/w) in a batch reactor for 6 h with a pressure of 2 MPa at 200 (hereafter referred to as Hydro200) and 250°C (hereafter referred to as Hydro250; SmartCarbon AG, Jettingen, Germany). Pyrochars were produced in a Pyreg reactor (PYREG GmbH, Dörth) for 0.75 h at 750°C (designated hereafter as Pyro750). Detailed information on char preparation and methods of analysis (e.g., specific surface area (SSA), pore volume, average pore size) can be found in Eibisch *et al.* (2013, 2015).

In order to simulate field aging, we compared unwashed chars with washed chars in the laboratory experiment. Washing was assumed to be capable of simulating aging of the char as initially bound nutrients or salts would be removed. Washing was carried out by shaking 4.5 g of biochar with 1 L of deionized water in an overhead shaker at 9 rpm for 4 h and thereafter the solution was filtered with pleated paper filter (grade: 3 hw; diameter: 150 mm; 65 g m^2) and filtrate (pyrochar or hydrochar) was dried for 24 h at 105°C. Washing effects were only studied in the pyrochar and hydrochar applied to silty loam mixtures, because highest nutrient leaching or adsorption effects were expected for this soil.

6.2.2 Field aging

Hydrochar and pyrochar produced from *Miscanthus* was used for the field incubation. The hydrochar was carbonized with water (1:10, w/w) in a tabular reactor (3 m^3) for 11 h with a pressure of 2 MPa at 200°C by AddLogicLabs/SmartCarbon (Jettingen, Germany). Citric acid was added as a catalyst for the dehydration process and to increase the C content in the solid product (Wang *et al.*, 2010). Pyrochars were produced in a Pyreg reactor for 0.75 h at 750°C. Analyses of general properties of the chars and raw material were carried out by Andrea Kruse (KIT, Karlsruhe). All chars were dried at 40°C and sieved <2 mm. Basic characteristics of feedstocks, pyrochars, and hydrochars for the laboratory batch and field incubation experiment are listed in Table 6.1.

Table 6.1 General properties of feedstock materials and chars used in the laboratory study ("Lab") and field incubation ("Field"). Data for chars used in the laboratory only derived from Eibisch *et al.* (2013, 2015) (n.d. indicates not determined).

Experiment	Feedstock	Char type	°C	pH ($CaCl_2$)	Ash content [%]	C [%]	N [%]	S [%]	O : C	H : C	P [%]	Ca [%]	Mg [%]	Na [%]	K [%]	SSA [$m^2\ g^{-1}$]	Pore volume [$cm^3\ g^{-1}$]	Average pore size [Å]
Lab	Digestates	Raw	–	–	11.9	41.9	1.57	0.28	0.87	0.14	1.28	0.87	0.66	0.05	2.88	8.6	0.03	61
		Hydrochar	200	6.2	10.3	53.8	2.59	0.30	0.46	0.10	1.23	1.39	0.48	0.03	0.98	13	0.09	192
		Hydrochar	250	5.7	13.6	61.8	2.98	0.22	0.29	0.08	1.56	1.60	0.85	0.03	1.41	2.8	0.02	167
		Pyrochar	750	9.8	46.0	69.7	< 1.0	0.18	0.17	0.04	2.51	2.91	1.12	0.24	8.10	448	0.28	12
	Miscanthus	Raw	–	–	2.9	45.6	< 1.0	0.07	0.86	0.13	0.09	0.22	0.07	0.01	0.53	1.0	0.01	154
		Hydrochar	200	4.6	3.9	58.0	< 1.0	0.07	0.46	0.10	0.13	0.30	0.05	0.02	0.27	5.2	0.05	180
		Hydrochar	250	4.2	4.5	69.0	< 1.0	0.07	0.27	0.08	0.17	0.30	0.06	0.01	0.30	5.8	0.05	179
		Pyrochar	750	9.0	15.0	76.9	< 1.0	0.12	0.10	0.02	0.41	1.14	0.30	0.18	2.12	279	0.19	14
	Woodchips	Raw	–	–	4.2	48.6	< 1.0	0.05	0.71	0.12	0.07	0.62	0.07	0.02	0.27	1.6	0.02	206
		Hydrochar	200	4.6	5.0	59.7	1.07	0.06	0.40	0.10	0.08	0.90	0.07	0.02	0.25	10	0.09	180
		Hydrochar	250	4.8	5.4	67.7	1.22	0.06	0.27	0.08	0.11	0.59	0.06	0.03	0.21	3.5	0.04	207
		Pyrochar	750	8.7	24.6	68.4	< 1.0	0.13	0.10	0.02	0.35	3.43	0.29	0.12	0.87	210	0.17	17
Field	*Miscanthus*	Raw	–	–	2.9	46.3	< 1.0	< 0.1	0.28	0.13	0.09	0.11	0.09	0.01	0.52	n.d.	n.d.	n.d.
		Hydrochar	200	3.8	3.9	63.8	< 1.0	< 0.1	0.15	0.08	0.13	0.11	0.13	0.21	0.13	n.d.	n.d.	n.d.
		Pyrochar	750	9.0	15.0	81.8	< 1.0	0.10	0.09	0.01	0.39	0.35	0.39	0.03	1.50	n.d.	n.d.	n.d.

For the investigation of the effect of aging of the chars in the field, chars were incubated in situ at three cropland sites in the North German lowland (mean annual temperature 8.8°C, around 600 mm precipitation). The three sites differ mainly in their soil texture (Table 6.2) and are located in Bortfeld (sandy loam (SL); 52°28' N, 10°41' E; 80 m a.s.l.), Volkmarsdorf (sandy loam (SL); 52°36' N, 10°89' E; 105 m a.s.l.), and Querenhorst (loamy sand (LS); 52°33' N, 10°96' E; 112 m a.s.l.). All sites were managed according to common regional practice with conventional tillage and fertilizing. Crop rotations were barley (2012), winter wheat (cover crop), and sugar beet (2013) (Querenhorst); barley (2012), mustard (cover crop), and sugar beet (2013) (Volkmarsdorf); and potatoes (2012) and sugar beet (2013) (Bortfeld). At all three sites, mini-plots (plot size: 70×70 cm; plot depth: 25 cm) were dug out in triplicate in March 2013, and the hydrochar and pyrochar were mixed into the soil in a cement mixer in an amount that aimed to double the soils' C content (corresponding to around 100 t ha^{-1} char). The experimental setup was a randomized plot design carried out in three rows for each site so that every row consisted of three treatments: (i) control (soil only), (ii) soil-hydrochar, and (iii) soil-pyrochar. In order to distinguish the soils' C contents from treated or non-treated soil, and to quantify any blending or attenuation with the surrounding soil, e.g., due to tillage, 105 g of zinc as an inert tracer was added to each treatment in the cement mixer (control, pyrochar-soil, hydrochar-soil). The mini-plots were not fenced off, so the farmers were able to manage the fields exactly like to the rest of the field.

Table 6.2 General properties of the soils used for the lab and field study (n.d. indicates not determined).

Experiment		Site	Soil type	Soil texture class	Sand [%]	Silt [%]	Clay [%]	C_{org} [%]	N_{tot} [%]	C / N	pH ($CaCl_2$)	CEC [$cmol_c\ kg^{-1}$]
Lab	1	Göttingen	Haplic Luvisol	Sandy loam	61.5	32.8	5.8	1.23	0.10	12.3	5.6	4.0
	2	Braunschweig	Haplic Cambisol	Silty loam	15.4	67.6	17.0	1.27	0.12	10.6	5.6	10.8
Field	1	Bortfeld	Loamic Cambisol	Sandy loam	57.0	37.1	5.9	0.93	0.13	7.3	6.4	n.d.
	2	Querenhorst	Arenic Planosol	Loamy sand	74.7	18.0	7.3	1.13	0.13	8.8	6.8	n.d.
	3	Volkmarsdorf	Cambic Planosol	Sandy loam	67.1	21.7	11.2	1.16	0.12	9.9	6.5	n.d.

Sampling was carried out twice: the first set of soil samples was taken in March 2013 right after mixing the soil with chars (T_0). After 7 months (October 2013) a second sampling was carried out (T_1). Soil samples were obtained by takeing five randomly distributed soil cores to a depth of 25 cm with a split-tube sampler (5 cm diameter) from each mini-plot. Afterwards, samples were dried at 40°C and sieved ≤ 2 mm. Zinc concentrations at T_0 and T_1 were used to calculate a correction factor F_Z, which determines the recovery rate of incubated biochars in the field study.

6.2.3 Batch sorption experiments

Soil–char mixtures used solely in the laboratory were produced by mixing 0.5 g of char with 10 g of soil in order to roughly double the soil's C content. Two soils were used for the char–soil mixtures: a silt loam (Blagodatskaya *et al.*, 2014) from a cropland site at the Thünen Institute in

Braunschweig, Germany (52°17' N, 10°26' E; 80 m a.s.l.), and a sandy loam from a cropland site of the University of Göttingen (Reinshof), Germany (51°28' N, 9°58' E; 205 m a.s.l.). The soil was dried at 105°C to inhibit any microbial activity and sieved <2 mm. The pH value of soils and chars was measured in 0.01 M $CaCl_2$ with a ratio of 1:5 (volume soil/volume solution). Carbon and N contents were determined using dry combustion with an elemental analyzer (LECO TruMac CN, LECO Corp., St. Joseph, MI, USA). Soil texture was determined by the combined sieve and pipette method.

Preliminary sorption kinetic experiments were conducted to determine the sorption equilibrium by shaking the batches for 4, 8, 12, 24, and 48 h at 9 rpm in an overhead shaker. Based on the results of the kinetic experiments, shaking time for the determination of the sorption isotherms was set to 24 h. Soil–char mixtures and 10.5 g of soil only (control) were added to 40 mL of a nutrient solution in a 50 mL plastic centrifuge tube. Six concentration levels of a nutrient solution containing several nutrients that were chosen in order to mimic a "typical" agricultural soil solution were used (Table 6.3).

Table 6.3 Ion concentrations of the nutrient solution and relative sorption rates of the two control soils (soil without application of char) at the six applied concentration levels.

	Ion	P1	P2	P3	P4	P5	P6
Nutrient solution	NO_3^--N [mg L^{-1}]	5	10	20	30	40	60
	NH_4^+-N [mg L^{-1}]	5	10	20	30	40	60
	PO_4^{3-}-P [mg L^{-1}]	1.25	2.5	5	7.5	10	15
Sandy loam	NO_3^--N [%]	−6	0.1	3	0	0.1	0
	NH_4^+-N [%]	15	15	16	15	16	11
	PO_4^{3-}-P [%]	−78	6	50	59	57	65
Silty loam	NO_3^--N [%]	−58	−28	−16	−8	−9	−5
	NH_4^+-N [%]	54	52	49	39	36	33
	PO_4^{3-}-P [%]	10	45	75	73	69	81

In addition, the pH value of the solution was adjusted to 6 by adding HCl. Triplicates were measured for each concentration level. The pH was measured immediately after shaking in the char/soil-solution mixtures. Thereafter, suspensions were centrifuged at 4500 rpm for 30 min. The supernatant was aspirated with a syringe and filtered through 0.45 µm membrane filters (CHROMAFIL PET-45/25 disposable syringe filters, Macherey-Nagel). The ion concentrations of the filtrates were analyzed using ion chromatography (IC) (METROHM 761) for anions (NO_3^-, PO_4^{3-}) and inductively coupled plasma chromatography (ICP) (ICS-90 Dionex/Thermo Fisher Scientific) for cations (NH_4^+). Moreover, contents of Ca^{2+}, Mg^{2+}, K^+, and SO_4^{2-} were also determined, and fitted isotherms can be found in Table S1 in the Supplement. The potential CEC of separate soil–char mixtures was determined following ISO 13536.

Soil–char mixtures from the field experiment were used directly in the batch sorption experiments (NO_3^-, NH_4^+, PO_4^{3-}), which were carried out as described above. To calculate the char adsorption effect relative to the control we used the following equations:

Relative adsorption of the control:

$$Q_{Ctrl} = \left(1 - \left(\frac{IC_{Ctrl}}{IC_{Blind}}\right)\right) \times 100 \quad \text{(Eq. 1)}$$

Relative adsorption of the char treatment to control:

$$Q_{Char} = \left(1 - \left(\frac{IC_{Char}}{IC_{Ctrl}}\right)\right) \times F_Z \times 100 \quad \text{(Eq. 2)}$$

Whereby F_Z was only used to calculate relative adsorption for field incubated chars. IC is the equilibrium ion content of the nutrient solution after shaking for blinds (IC_{Blind}), control (IC_{Ctrl}) or soil-char mixtures (IC_{Char}).

Statistical Analyses

Adsorption data were fit to Freundlich and linear adsorption isotherms:

Freundlich isotherm: $Q_e = K_F \cdot IC^{1/n}$ (Eq. 3)

Linear isotherm: $Q_e = a \cdot IC + Y_0$ (Eq. 4)

Q_e is the amount of ion adsorbed, while IC is the concentration in the solution after 24 h equilibration. A positive Q_e indicates adsorption of ions in the nutrient solution on an adsorbent and a negative Q_e desorption from adsorbent to the nutrient solution.

Logarithmized equilibrium-concentration and log adsorbed amount was used to calculate the Freundlich sorption partitioning coefficients (K_F) and the Freundlich exponents ($\frac{1}{n}$) following nonlinear fitting. For linear isotherm, Y_0 is the intercept.

The Akaike information criterion (AIC) was used to select the best fitting isothermal model. Significance of treatment effects on shape of isotherms was tested using two procedures:

ii) If, for two treatments, the same model type resulted in the best fit, their difference was tested with a likelihood-ratio test. It was tested whether fitting the model to the data separately resulted in a better fit than fitting the model to the combined data. If the separately fitted model resulted in a better fit than the combined model, treatments were different with their corresponding p-value. This test could only be conducted if it was numerically possible to fit the model to the combined data.

ii) Generalized additive models (GAM, R package *gam*; Hastie, 2013), including and excluding treatment as a predictor, were fitted and compared using analysis of deviance with χ^2 statistics. All *p* values were adjusted for multiple testing using the procedure of Benjamini and Hochberg (1995). All statistical analyses were conducted using R 3.1.1 (R Core Team, 2014). The results of the statistical analyses can be found in the Supplement (Tables S1, S3, S5, S7, and S8). Significant differences between washed an unwashed chars were tested with the unpaired *t*-test.

6.3 Results

6.3.1 Physicochemical properties of the chars

The pH values of the hydrochars were acidic ranging from 3.8 to 6.2 and 4.2 to 5.7 for Hydro200 (hydrochars produced at 200°C) and Hydro250 (hydrochars produced at 250°C), respectively (Table 6.1). The pH values of pyro750 (pyrochars produced at 750°C) were alkaline (8.7 to 9.8). The ash content increased with increasing carbonization temperature and was highest for pyrochars from woodchips (24.6%). Generally, woodchips had the highest C concentration (48.6% C) as a raw material, but after carbonization, Pyro750 from *Miscanthus* had the highest C concentrations (Lab: 76.9% C; Field: 81.8% C). The highest amounts of total N and P were found in Hydro200 and Hydro250 from digestates. After carbonization, highest SSA was observed for pyrochars and decreased in the order Pyro750 > Hydro200 > Hydro250 (Table 6.1). Pyro750 showed the highest pore volume, followed by Hydro200 and Hydro250. In general, Pyro750 showed smaller average pore size than Hydro200 and 250 by a factor of 10.

6.3.2 Influence of soil, feedstock, and carbonization type on nutrient sorption (laboratory experiments)

Figures 6.1, 6.2, and 6.3 show the relative change in ion concentrations of the char treatments from the three feedstocks (triangles: *Miscanthus*; circles: digestates; squares: woodchips) to the control (0% line) at all applied nutrient concentration levels. Positive values correspond to adsorption and negative values to leaching.

Sorption of nitrate

The pure sandy loam (control in Table 6.3) showed neither NO_3^- sorption nor release (all data points are around 0 %). In contrast, the pure silty loam tended towards a high NO_3^- release of around 60 %: at the lowest concentration level of the nutrient solution (Table 6.3). This release decreased to 5% with increasing concentrations of the nutrient solution. Mixing soil with Pyro750 significantly reduced NO_3^- leaching, independent of the soil and feedstock used (Figure 6.1a,b). The relative amount of adsorbed NO_3^- in pyrocharamended soils was higher in sandy loam than in silty loam. At the lowest concentration level of the nutrient solution, application of Pyro750 raised NO_3^-adsorption

between 2 and 15% (silty loam) and 7 and 30% (sandy loam) compared to the respective control soil (Figure 6.1a, b). The relative adsorption on Pyro750 decreased with increasing nutrient-solution concentration to 5–12 %. For both soil types, the fitted isotherms for Pyro750 were significantly different from the control ($p \leq 0.01$) and to both Hydro200 and Hydro250 ($p \leq 0.01$). Further, isotherms of NO_3^- adsorption by Pyro750 mixed with sandy loam were significantly different to those of silt loam ($p \leq 0.01$). Further, the effects of nutrient retention in Pyro750 mixtures compared to the control soil depended on the carbonized feedstock ($p \leq 0.01$; Figure 6.1a, b). Adsorption increased in the order digestates (3–8 %) < *Miscanthus* (10–14 %) ≤ woodchips (10–15 %) in both soil types depending on the nutrient-solution concentration. Addition of hydrochar to the soils had no effect on NO_3^- adsorption irrespective of the carbonization temperature used, feedstock, or soil type (Figure 6.1c, d).

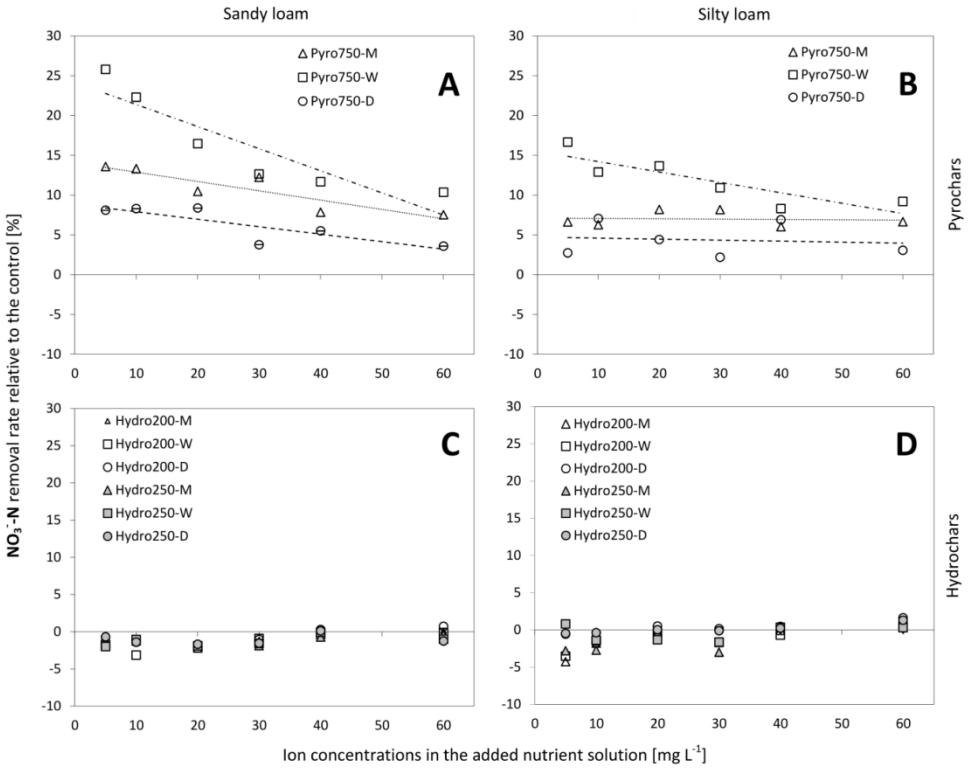

Figure 6.1 Mean NO_3^--N removal rates in soil–char composites relative to the control [%] (the respective soil with no char added) for pyrochars (Pyro750) **(a, b)** and hydrochars derived at 200°C (Hydro200) and 250°C (Hydro250) **(c, d)** from *Miscanthus* (M), woodchips (W), and digestates (D) mixed with the sandy and silty loam soil at the six nutrient-solution levels (n=3).

Sorption of ammonium

The NH_4^+ sorption in the soils without char was around 3–4 times higher for the silty loam than the sandy loam (Table 6.3). The silty loam adsorbed around 55% at the first concentration level, and adsorption decreased to 32% with increasing nutrient concentrations, while the sandy loam adsorbed around 15% at all concentration levels.

Comparison of fitted isotherms of both soils mixed with Pyro750 showed significant differences between sandy loam and silty loam ($p \leq 0.01$). The effect of feedstock on relative NH_4^+ adsorption was soil-dependent and significant for both soils (Figure 6.2a, b; $p \leq 0.05$). While NH_4^+ adsorption was enhanced by the application of pyrochar in the sandy loam, pyrochar addition to the silty loam showed no effect or even led to leaching. Further, the effect of the feedstock differed between the two soils investigated: when added to sandy loam, pyrochar application increased the adsorption relative to control. Depending on the nutrient solution concentration, the relative adsorption increased in the order *Miscanthus* (~0 %) < woodchips (2–8 %) < digestate (7–17 %) ($p \leq 0.01$; Fig. 2a). For the silty loam, the effect of pyrochar addition on the relative NH_4^+ adsorption was woodchips (~0 %) < *Miscanthus* (0–20 %) < digestates (up to -45% at the first two NH_4^+ concentration levels; Figure 6.2b) only at the first three nutrient concentration levels.

Application of hydrochars to either soil type showed no consistent effects. These ranged from leaching to adsorption with relative values between +10 and -20 %, respectively (Figure 6.2c, d). In general, NH_4^+ adsorption by the control soil was significantly different to that in the soil amended with hydrochars ($p \leq 0.01$) for both sandy loam and silty loam. For Hydro200, NH_4^+ adsorption was close to zero when compared to the control at all concentration levels. A significant relative adsorption effect was observed for only some concentration points (Figure 6.2c). Hydro250 showed both NH_4^+ release at the lowest concentration level and little adsorption of NH_4^+ at the higher concentration levels reaching up to about 10 % (Figure 6.2d). The fitted isotherms for Pyro750 are significantly different from those for hydrochars and pure soil (depending on soil type), but there were no differences between Hydro200 and Hydro250. For hydrochars, no effect of feedstock on NHc_4 adsorption was observed except for lower adsorption of Hydro200 from digestates compared to *Miscanthus* and woodchips ($p \leq 0.01$).

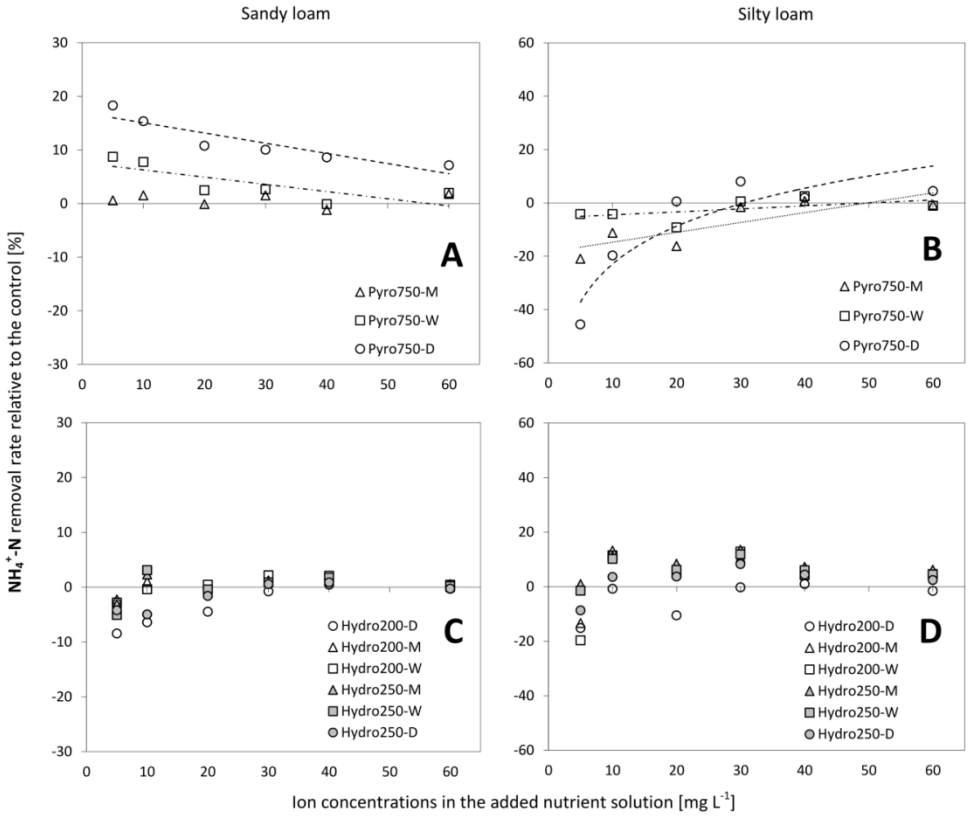

Figure 6.2 Mean NH_4^+-N removal rates in soil–char composites relative to the control [%] (the respective soil with no char added) for pyrochars (Pyro750) **(a, b)** and hydrochars derived at 200°C (Hydro200) and 250°C (Hydro250) **(c, d)** from *Miscanthus* (M), woodchips (W), and digestates (D) mixed with the sandy and silty loam soil at the six nutrient-solution levels (n=3).

Sorption of phosphorus

The sandy loam leached PO_4^{3-} at the lowest concentration level, but this changed to 65% adsorption at higher levels, while the silt loam adsorbed up to 80% at all PO_4^{3-} concentration levels (Figure 6.3a, b).

Only pyrochars enhanced PO_4^{3-} adsorption. The fitted isotherms for pyrochars were significantly different from the respective control soil ($p \leq 0.01$), but this effect strongly depended on feedstock material (digestates (only leaching) < *Miscanthus* <woodchips) and soil (silty loam < sandy loam). For Pyro750, there were significant ($p \leq 0.01$) differences between feedstocks: Pyro750 from *Miscanthus* mixed with the sandy loam resulted in a relative PO_4^{3-} adsorption of 20–30% (Figure 6.3a) but 20% less adsorption (leaching) when mixed with the silty loam (Figure 6.3b). Woodchip pyrochar was most effective in adsorbing PO_4^{3-} (15–40%for the silty loam and 60–70% for the sandy loam) during all nutrient-solution concentrations. However, pyrochar from digestates showed strong leaching in both sandy and silty loam (Figure 6.3a, b). Adding Pyro750 from digestates enriched the nutrient solution by up to 1000% (sandy loam) and 1300% (silty loam) at the lowest PO_4^{3-}-P concentration level, and still by 100% at the highest PO_4^{3-}-P concentration. Although relative PO_4^{3-} adsorption was higher in the sandy loam than in the silty loam after addition of Pyro750, these differences were not significant.

The addition of hydrochar (both Hydro200 and Hydro250) to soil mainly led to leaching of PO_4^{3-} from chars or had no consistent effect (Figure 6.3c, d). Fitted isotherms showed significant differences between Hydro200 and Pyro750 ($p \leq 0.01$) but no differences to control or Hydro250. The adsorption of the soil was lowered by maximum values of around 40% for the sandy loam and 60% for the silty loam due to PO_4^{3-} leaching. Values depended on the feedstock used and soil type ($p \leq 0.01$). Again, the effect of feedstock (or any effect at all) was less pronounced for hydrochars than pyrochars: hydrochars from digestates tended to reduce the relative PO_4^{3-} adsorption by leaching. Mixing soil with Hydro200 and Hydro250 from *Miscanthus* and woodchips resulted in no effect on PO_4^{3-} adsorption (Figure 6.3c). For both soil types, differences between Hydro200 from digestates to *Miscanthus* and to woodchips were significant ($p \leq 0.01$). For Hydro250, only digestates to *Miscanthus* and to woodchips were significantly different ($p \leq 0.01$) in the sandy loam.

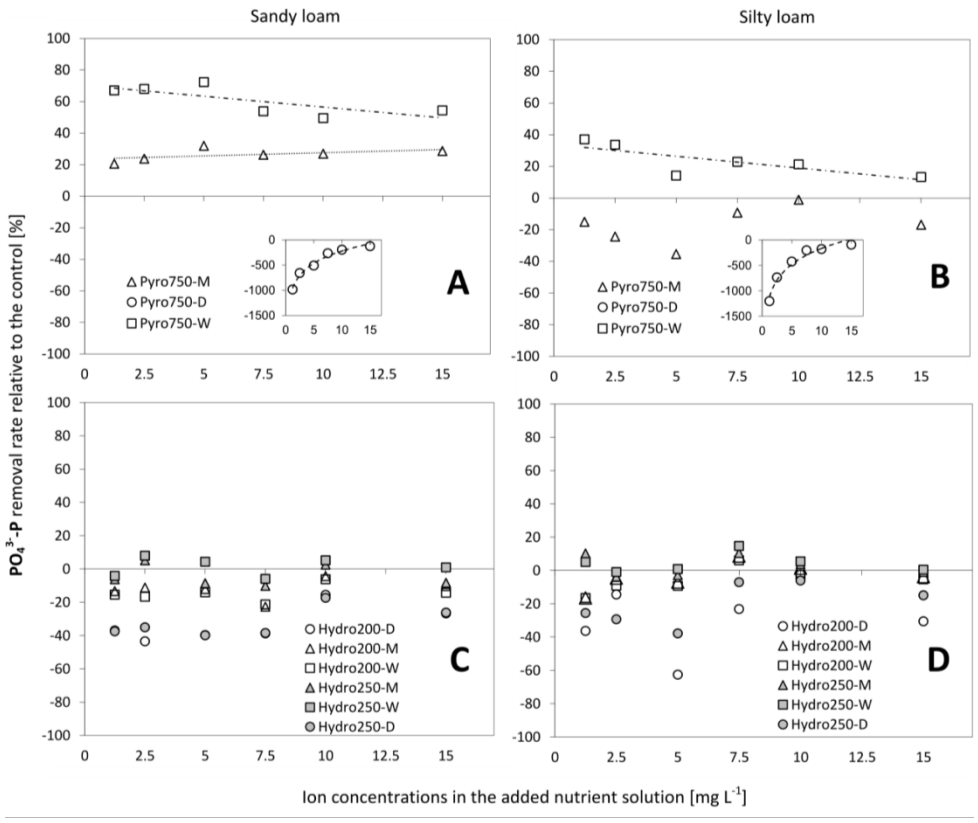

Figure 6.3 Mean PO_4^{3-}-P removal rates in soil–char composites relative to the control [%] (the respective soil with no char added) for pyrochars (Pyro750) **(a, b)** and hydrochars derived at 200°C (Hydro200) and 250°C (Hydro250) **(c, d)** from *Miscanthus* (M), woodchips (W), and digestates (D) mixed with the sandy and silty loam soil at the six nutrient-solution levels (n=3).

The effect of char aging on nutrient sorption (field experiment)

At all three experimental sites, NO_3^- was leached from pure soil with no char addition (control; data not shown). However, leaching was less pronounced at T_1 than T_0 ($p \leq 0.01$). Amending the soils with char led to adsorption of NO_3^- for both pyrochar and hydrochar at all experimental sites (Figure 6.4a–c). However, adsorption was higher for pyrochars than hydrochars ($p \leq 0.01$). Pyrochar reduced NO_3^- leaching by up to 58% relative to the control soil at the lowest nutrient-solution concentration, while hydrochar reduced leaching by up to 25% (Figure 6.4a–c). After 7 months of aging in the field (T_1), adsorption by pyrochars decreased by 60 to 80 %, often ending up with no nutrient retention relative to control ($p \leq 0.01$; Figure 6.4a–c). Slight differences were observed between the three investigated sites, but these were not significant. The effect of hydrochar addition diminished in a similar way after 7 months: relative adsorption decreased by 10 to 100 %, ending up with no nutrient retention at Bortfeld (Figure 6.4a) or even nutrient leaching (site Querenhorst and site Volkmarsdorf, Figure 6.4b, c), as compared to the nonamended control soil. In four of our six cases, sorption effects of both pyrochar and hydrochar were found to be significantly different for the aged biochar–soil mixture as compared to fresh biochars mixed into soils.

Highest adsorption of NH_4^+ was observed for fresh chars (T_0) and adsorption was higher for pyrochar than for hydrochar at two sites (Bortfeld and Volkmarsdorf, $p \leq 0.01$) but was similar at the third site (Querenhorst) (Figure 6.4d–f). For soils amended with fresh pyrochar, adsorption of NH_4^+ was up to 40% higher than observed for the control soil. After 7 months, NH_4^+ adsorption of pyrochar–soil mixtures was significantly lower at all experimental sites than right after the char application ($p \leq 0.01$). Little relative NH_4^+ adsorption was found for fresh hydrochar and for aged hydrochar in the field. The relatively low adsorption capacity of hydrochars sometimes even changes to NH_4^+ leaching. The effect of pyrochar aging on PO_4^{3-} adoption was different from the other nutrients: aging increased the PO_4^{3-} retention capacity of pyrochar soil mixtures at all three sites from leaching or no effect (T_0) to adsorption (T_1) (Figure 6.4g–i). The effect of hydrochar on PO_4^{3-} was minor. Hydrochar was a source for PO_4^{3-} in most soils with no consistent changes due to char aging.

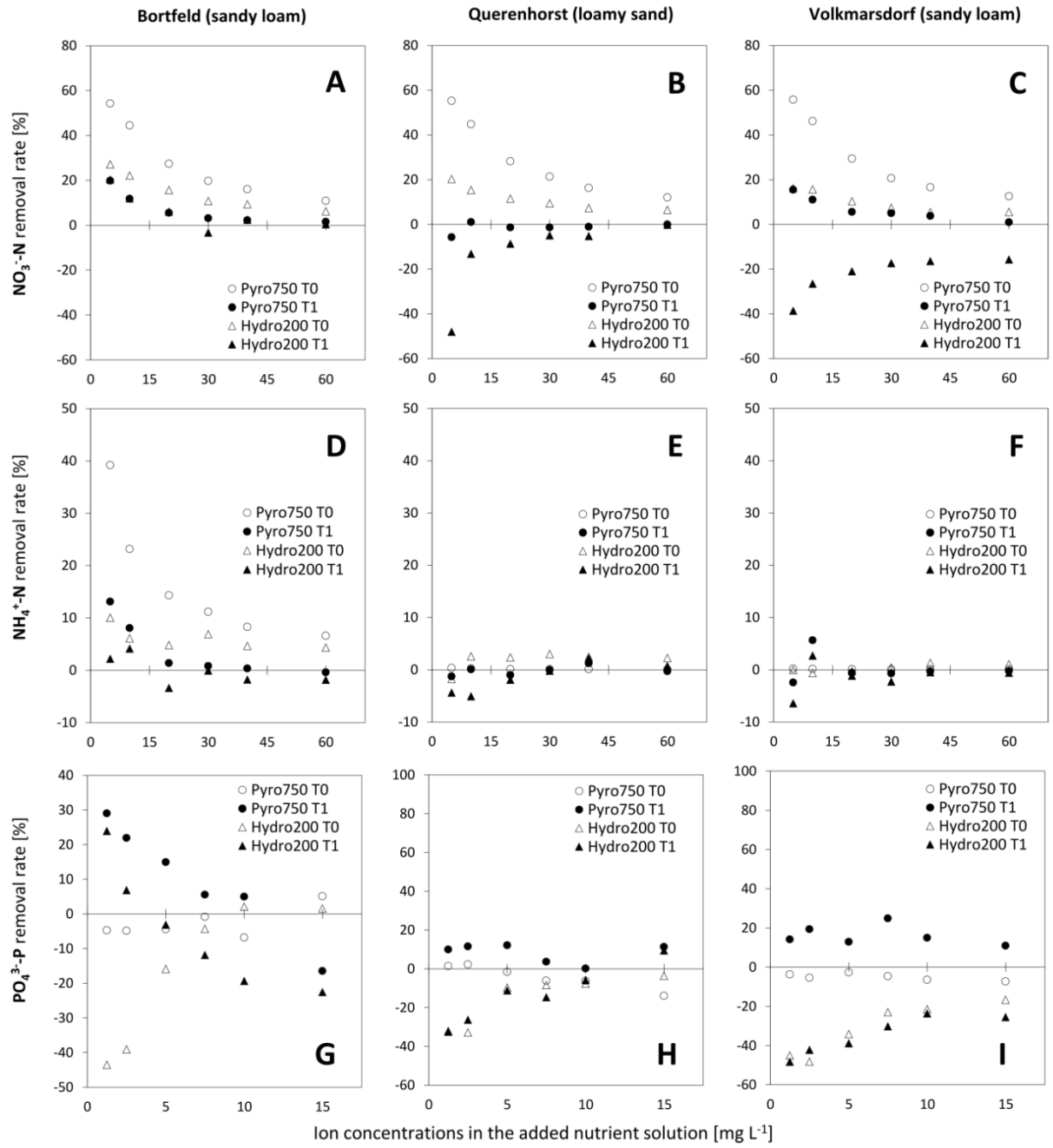

Figure 6.4 Mean NO_3^--N **(a–c)**, NH_4^+-N **(d–f)**, and PO_4^{3-}-P **(g–i)** removal rate relative to the control for fresh (T_0) and degraded (T_1) pyrochars of the field experiment (for all treatments, n=3). Test statistics can be found in Tables S5, S7, and S8.

Effects of char preparation (washing)

Washing was carried out in order to reduce initial leaching effects from chars – i.e. it was assumed that nutrients and salts were removed from the surface of the chars by washing. Figure 6.5 shows relative changes in ion concentration to control (0% line; IC_{Blind}: 20.23 mg N L^{-1}; IC_{Ctrl}: 23.37 mg N L^{-1}) at nutrient concentration level P3 (Table 6.3). Positive (negative) values indicate higher (lower) removal of ions from nutrient solution compared to control due to adsorption or leaching, respectively. Washing of both Hydro200 and Hydro250 increased the pH of the nutrient solution by 0.1 to 0.2 pH units, whereas washing of Pyro750 decreased the pH by 0.2 to 0.4 units. The sorption behavior of both pyrochars and hydrochars significantly changed due to washing (Figure 6.5). Washing increased the potential NO_3^- adsorption of pyrochars by 3–4% ($p \leq 0.05$; Figure 6.5a). For hydrochars, a similar effect was only observed for Hydro200 from digestates, changing the soil–hydrochar mixture from a NO_3^- source (leaching) into a sink (absorption) ($p \leq 0.05$). In the case of NH_4^+ , a decrease in net leaching was observed for all treatments (Figure 6.5b). For most hydrochars, washing even turned soil–hydrochar mixtures from NH_4^+ sources (leaching) into net sinks (adsorption) (Figure 6.5b). Strongest reductions in leaching were observed for Pyro750 (-37 %) and Hydro200 from digestates (-35 %). Washing effects on PO_4^{3-} sorption were inconsistent. Pyro750 showed increased PO_4^{3-} leaching (digestates), decreased adsorption (woodchips), and leaching instead of sorption (*Miscanthus*) (Figure 6.5c). In the case of Hydro200 from digestates, PO_4^{3-} leaching was reduced by up to -950 %. For all other hydrochar mixtures, washing reduced both PO_4^{3-} leaching and sorption close to zero. Overall, washing seemed to be an effective measure to reduce the ion leaching of those ions that were adsorbed to the surface of fresh chars.

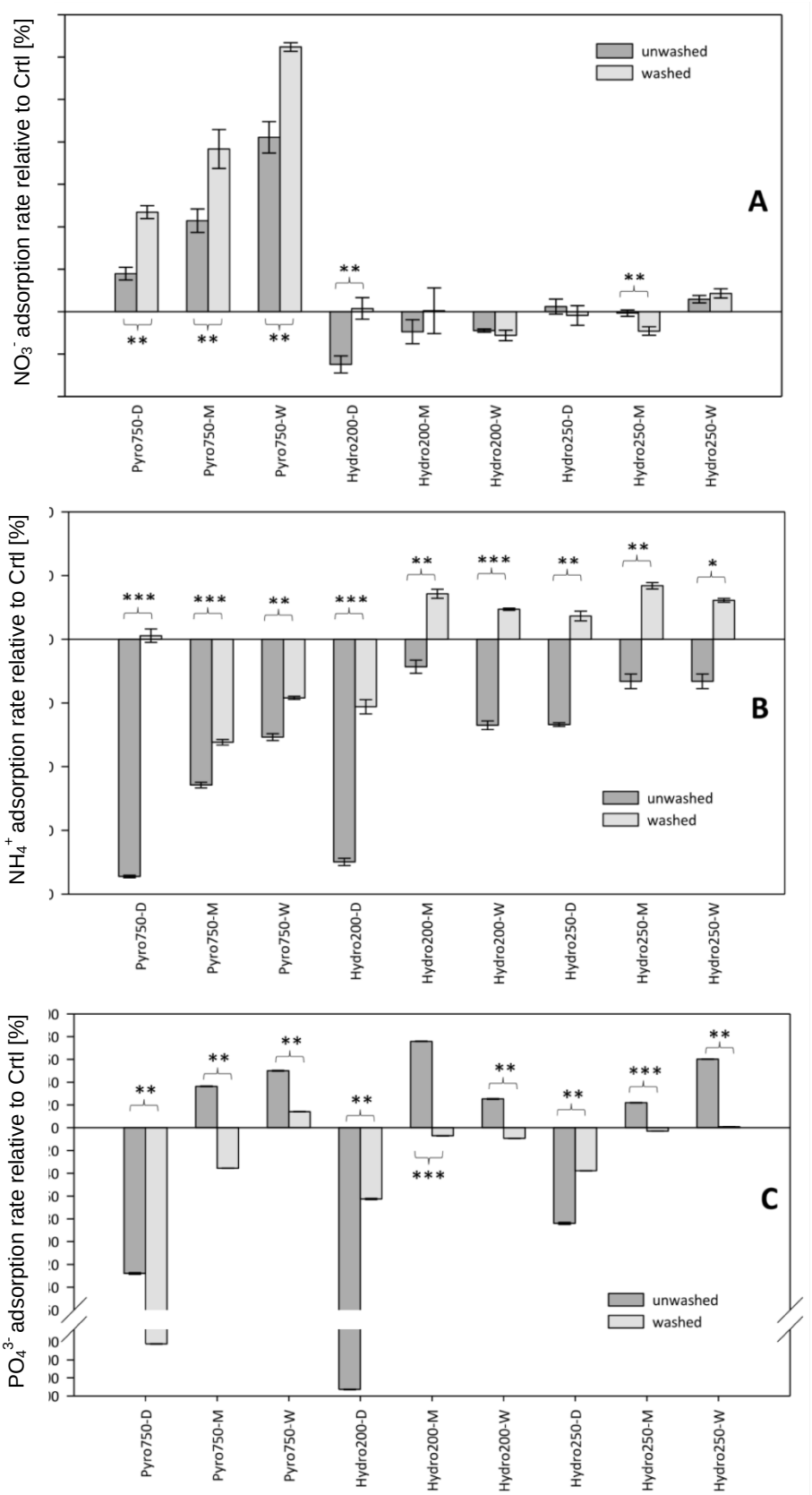

Figure 6.5 **(a)** NO_3^- , **(b)** NH_4^+ , and **(c)** PO_4^{3-} removal rates in soil–char composites relative to the control (silt loam without char) for washed and unwashed pyrochars (Pyro750) and hydrochars derived at 200°C (Hydro200) and 250°C (Hydro250) from *Miscanthus* (M), woodchips (W), and digestates (D). Significant differences between washed and unwashed chars were tested with the unpaired t-test. p values are indicating by *** < 0.01, ** < 0.05, and * < 0.1 (for each treatment n=3, means±SE).

6.4 Discussion

6.4.1 Char-induced effects on nutrient sorption: effects of carbonization process and feedstock material (laboratory experiments)

Pyrochars and hydrochars showed general differences in their sorption behavior. In most cases, pyrochars removed NO_3^-, NH_4^+, and PO_4^{3-} from soil solution. This is in line with previous studies (Hale *et al.*, 2013; Sarkhot *et al.*, 2013; Yao *et al.*, 2012). Hydrochars showed marginal or no sorptive effect on NO_3^-, NH_4^+, and PO_4^{3-}. Similar to our findings, Yao *et al.* (2012) found no sorptive effect of hydrochar from peanut hulls on NO_3^-, NH_4^+, and PO_4^{3-}. Previous studies indicate that increasing carbonization temperature results in higher SSA of the produced char (Cantrell *et al.*, 2012), which in turn leads to higher NO_3^- adsorption (Hale *et al.*, 2013; Yao *et al.*, 2012; Lehmann and Joseph, 2009). However, the AIC was used to select the best-fitting isothermal model. For NO_3^- sorption on pyrochars, AIC prefers the fitted linear model rather than the Freundlich isotherm, which indicates a non-saturated surface of chars at increasing ion concentration of the nutrient solution. This contradicts previous studies which prefer Freundlich or Langmuir (Hale *et al.*, 2013; Mizuta *et al.*, 2004). In most cases, hydrochars showed no sorptive effect, but, in particular for hydrochars from digestates, PO_4^{3-} release into aqueous solution was partly observed. This finding is corroborated by Yao *et al.* (2012), who also found 4% PO_4^{3-} leaching into aqueous solution in sandy soil mixed with hydrochar from peanut hull. The digestate feedstock and digestate carbonized to pyrochar and hydrochar contained 10 times more phosphorus (2.51 %, Table 6.1) than the chars produced from the other two feedstock materials, which explains the high PO_4^{3-} leaching.

Besides carbonization process, the feedstock material had a marked influence on the sorption behavior, which is in accordance with findings from other studies: while NO_3^- sorption was observed for pyrochar from Monterey pine (Knowles *et al.*, 2011), sugarcane bagasse, and bamboo (Yao *et al.*, 2012; Mizuta *et al.*, 2004), pyrochar from pure washed cacao shell and corn cob without soil led to NO_3^- release (Hale *et al.*, 2013). This implies strong adsorption capacity variations with carbonized feedstock. The three carbonized feedstocks we tested (*Miscanthus*, digestates, and woodchips) for pyrochars showed high correlations between NO_3^- adsorption and logarithmized SSA $R^2 = 0.57$; $p \leq 0.05$ for amended loamy soil/0.64; $p \leq 0.01$ amended sandy soil), and average pore size ($R^2 = 0.64$ for amended loamy soil/0.72 for amended sandy soil; both $p \leq 0.01$). We also found strong correlations between H:C (indicates carbonization temperature) and NO_3^- adsorption ($R^2 = 0.65$ for amended loamy/0.75 sandy soil respectively; both $p \leq 0.01$). The NH_4^+ sorption is strongly nonlinear with increasing solution concentration (Freundlich coefficient n = 1.1–1.5), which indicates a limited number of cation exchange sites of char (Hale *et al.*, 2013). For all pyrochars, irrespective of feedstock, pore volume ($R^2 = 0.52$, $p \leq 0.01$), and ash content ($R^2 = 0.66$, $p \leq 0.01$) correlated with NH_4^+ adsorption. No saturation was found for PO_4^{3-}, with increasing

solution concentration, especially evident for pyrochars from *Miscanthus* and also from woodchips for the concentration range used (2.5–15 mg P L^{-1}). This indicates that pyrochars could remove more PO_4^{3-} at higher solution concentrations, which is supported by Sarkhot *et al.* (2013), who tested 2 g of pyrolyzed hardwood chars (without soil) in 40 mL of nutrient solution at higher solution concentrations in comparison to ours (up to 50 mg P L^{-1}).

Generally, nutrient retention potential of char is a result of cation or anion exchange combined with the large surface area, internal porosity and polar and nonpolar surface sites of functional groups (Hale *et al.*, 2013; Laird *et al.*, 2010; Lehmann and Joseph, 2009). Additionally, Keiluweit and Kleber (2009) reviewed cyclic aromatic π systems which showed specific π–electron donor–acceptor (EDA) interactions (i.e., cation–π, hydrogen–π, π–π EDA, and polar–π interaction) with bonding energies between 4 and 167 kJ mol^{-1} to nutrients. Thus, chars' surface charge is assumed to be negative, resulting in low anion exchange capacity and repellence of NO_3^- and PO_4^{3-} (Hale *et al.*, 2013; Mukherjee *et al.*, 2011). However, our results and results from previous studies showed anion adsorption, the processes of which are not yet fully understood. Chun *et al.* (2004) and Chen *et al.* (2008) disproved the ability of PO_4^{3-} ions to bind with negatively charged char surface functional groups like hydroxyls, carbonyls, carboxyls, and phenolics. However, Sarkhot *et al.* (2013) proposed that the exchange of surface hydroxyl groups on biochar with PO_4^{3-} induces a pH-controlled anion sorption capacity. Another mechanism is the ability of PO_4^{3-} ions to form bridge bonds using the residual charge of electrostatically attracted or ligand-bonded multivalent cations (Ca^{2+}, Mg^{2+}, Al^{3+},Fe^{3+}) (Mukherjee *et al.*, 2011). We could not directly verify this assumption in our study because Ca^{2+} and Mg^{2+} were strongly leached (see Supplement; Table S1), but we suspect that the residual charge of electrostatically attracted cations binds PO_4^{3-} in the double-layer sheet. Klasson *et al.* (2014) showed that pore-blocking ash content could be reduced by washing chars with rainwater, thereby increasing micropore volume, total pore volume, and SSA. Hale *et al.* (2013) suggest enhanced PO_4^{3-} sorption due to increasing availability of binding sites on char's surface after washing. However, in our lab experiment we did not find increasing PO_4^{3-} adsorption due to washing for any type of char.We assume that primary bonding agents for PO_4^{3-} (Ca^{2+}, Mg^{2+}, Al^{3+},Fe^{3+}) are leached out, which results in no adsorption to the char surface. Secondly, PO_4^{3-} compounds from the char matrix itself are rinsed.

6.4.2 Soil-induced effect on nutrient sorption (laboratory experiments)

Our results show that pyrochars could remove NO_3^- and PO_4^{3-} from soil solution when added to different soils (sandy and silty loam). NH_4^+ was retained only in the sandy loam which confirms the findings of Yao *et al.* (2012), who also mixed pyrochars with a sandy soil. For pyrochars mixed with loamy soil, we found reduced sorption capacity for NO_3^- , NH_4^+ , and PO_4^{3-}, which is corroborated by Hale *et al.* (2011), who reported a reduction in the sorption capacity of chars mixed

with a fine-loamy soil. Hydrochars showed little (silty loam) or no (sandy loam) sorptive effect on NO_3^-, NH_4^+, and PO_4^{3-}.

The adsorption capacity of chars for nutrients interacts with the amended soil type. Generally, soil's adsorption capacity for NO_3^-, NH_4^+, and PO_4^{3-} is determined by pH, CEC, AEC, SSA, organic matter content, and soil texture. Hale *et al.* (2011) suggest a decreased reduction in the sorption capacity of chars caused by blocking of sorption sites by DOC, which could leach out from soil and may adsorb to chars. The solubility of DOC can be increased by increasing negative charge on the DOC due to a raised pH through char application to soils (Alling *et al.*, 2014). In our study, application of pyrochars led to a stronger rise in pH in the silty loam than in the sandy loam (Table S2). According to Hale *et al.* (2011), this could have induced higher DOC solubility in the sandy loam and the leached DOC was adsorbed by pyrochars, resulting in blocked binding sites. Further, the soils tested in this study differed strongly in their texture and CEC. The silty loam contained higher amounts of multi-layer clay minerals, which led to higher adsorption competition between char and clay mineral surfaces. Ersahin *et al.* (2006) report SSA between 46.5 and 90.4 as well as 20.6 and 61.95 $m^2\ g^{-1}$ for silty loams and loamy sands, respectively. The pyrochars we tested had SSAs between 210 and 448 $m^2\ g^{-1}$, which are considerably higher than the SSA of the soils used. The difference in SSA between pyrochar and soil was larger for the sandy loam than the silty loam. This resulted in stronger adsorption potential for ions from sandy loam or nutrient solution to the pyrochars. However, the larger SSA of the silty loam enhanced the adsorption competition for ions between loamy sand and pyrochars. In addition, ions from the nutrient solution are more attracted to the silty loam than to the sandy loam or to the pyrochars. Furthermore, soil-bound ions such as NO_3^-, K^+, Mg^{2+}, and Ca^{2+} were leached from the silty loam and were directly adsorbed by pyrochars, suggesting that this direct adsorption may result in occupied binding sites on the pyrochars, which led to no or less adsorption of NO_3^-, NH_4^+, and PO_4^{3-} from the nutrient solution.

6.4.3 Effect of char aging on nutrient sorption (field and laboratory experiment)

The ability of both pyrochar and hydrochar to adsorb NO_3^- and NH_4^+ from soil solution was stronger for fresh char as compared to aged char (i.e., after 7 months of field incubation). This was an unexpected behavior and often led to a complete loss of the char's nutrient retention capacity and has rarely been studied to date. Since the overall adsorption capacity of hydrochar observed in our study was small, the aging effect was also less pronounced compared to pyrochars. For hydrochars, other studies reported the physical structure and chemical properties result in a lower recalcitrance towards microbial degradation compared to pyrochars (Bargmann *et al.*, 2014a; Hale *et al.*, 2011; Steinbeiss *et al.*, 2009). Explanations for the decreasing nitrogen adsorption capacity of pyrochar may include the following: (a) binding sites of both types of char may be blocked with organic matter or mineral particles such as clay, and (b) binding sites of pyrochar may be reduced by

microbial degradation changing the char's surface properties, which in turn leads to a diminished number of negatively charged binding sites (Cheng *et al.*, 2008; Cheng *et al.*, 2006; Glaser *et al.*, 2000). However, for our study, we could not explain decreasing adsorption with these mechanisms.

Such a trend of decreasing adsorption capacity over time was also reported by Bargmann *et al.* (2014b), who incubated 2 and 4% hydrochars from beetroot chips (*Beta vulgaris*) with a loamy soil for 8 weeks in the laboratory. A diminished number of negatively charged binding sites may result in higher leaching of positively charged ions (such as NH_4^+ , Ca^{2+}, Mg^{2+}, and K^+). In our experiment, the adsorption rate of NH_4^+ was reduced over time and Ca^{2+} as well as Mg^{2+} showed higher leaching after 7 months (Table S5). The chars used in the field experiment had not been pretreated by washing. The increased adsorption capacity of char for PO_4^{3-} may thus be partly a result of initially bound PO_4^{3-} that was leached from fresh chars (T_0) and was leached less after 7 months (T_1). However, in our laboratory experiment, washing did not reduce PO_4^{3-} leaching but increased the adsorption. Phosphate adsorption on char depends strongly on pH. For the chars we used, the effect on pH in the nutrient solution was lower for washed than unwashed chars.

6.5 Conclusions

The nutrient retention potential of chars (i.e., nitrate, ammonium, and phosphate) differs strongly with nutrient, char type (hydrochar vs. pyrochar), and type of carbonized feedstock, as well as amended soil type. Among nine different types of chars tested in a laboratory batch experiment, only pyrochars showed the ability to effectively retain nitrate, ammonium, and phosphate. Moreover, the nutrient retention effect seems to be of very limited duration. After 7 months in the field, around 60 to 80% of the adsorption capacity of pyrochar was lost. Underlying mechanisms are poorly understood, but our results cast doubt on the efficiency of char application to minimize the problems of nutrient leaching from agricultural soils to the groundwater and adjacent ecosystems.

6.6 References

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CHAPTER 7 MITIGATION OF AMMONIA EMISSIONS FROM MANURES: ACIDIFICATION IS MORE EFFECTIVE THAN CHAR APPLICATION

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Abstract

Nitrogen loss as ammonia from agricultural systems is one of the major sources of atmospheric pollutants and is responsible for more than 50% of global ammonia emissions. Ammonia volatilization from manures may be reduced with the addition of chars derived from pyrolysis (pyrochars) or hydrothermal carbonization (hydrochars). In a lab-incubation experiment we investigated the effect of pyrochar and hydrochar produced from biomass of *Miscanthus* mixed with manure (poultry litter and cattle slurry) on ammonia volatilization. We conduct manure treatments with and without acidification to shift the ammonia/ammonium-equilibrium towards ammonium. This allows us to distinguish between an additional pH-effect induced by chars or from ammonium adsorption in an ammonia-sorption experiment. Ammonia volatilization was higher in poultry litter than in cattle slurry treatments. Pyrochars slightly increased ammonia emissions from both manures due to their alkaline pH. In contrast, hydrochars decreased the pH and consequently slightly reduced the ammonia emissions. We found no ammonium adsorption effects due to char additions. Thus, the efficiency of char additions to reduce nitrogen losses as ammonia from manures is minor in comparison to manure acidification.

7.1 Introduction

Agricultural systems are among the major sources of atmospheric pollutants including ammonia (NH_3). They are responsible for more than 90% of total NH_3 emissions in Europe (Erisman *et al.*, 2008) and more than 50% of the global NH_3 emissions (Bouwman *et al.*, 1997). Atmospheric deposition of nitrogen (N) can destabilize natural and semi-natural terrestrial ecosystems, where biomass growth is often N limited and native species are adapted to low N availability. Application of organic manures such as cattle slurry or poultry litter to agricultural soils is one of the major drivers for various threats to the environment (Beusen *et al.*, 2008). Loss of N from manures may induce soil acidification, increase direct and indirect greenhouse gas emissions (Karaca *et al.*, 2004) and cause eutrophication of the receiving water bodies. In Europe, the reduction of NH_3 emissions has been increasing in relevance for more than a decade. In the "Thematic Strategy on Air Pollution" (CEC, 2005), the European Comission aimed at reducing around 30% of agricultural NH_3 emissions in the EU25 by 2020 as compared to 2000. Therefore, besides manure acidification (Kai *et al.*, 2008) and adjusted manure application methods (Webb *et al.*, 2010; Flessa and Beese, 2000), new technologies are required to decrease NH_3-volatilization from organic manure applied to soils and enhance the nutrient use efficiency of agricultural plant production. The amendment of manure with chars is proposed as one promising option to decrease NH_3-volatilization, retain nutrients and prevent leaching (Lehmann and Joseph, 2009).

Chars are the solid charcoal product of thermal conversion of a variety of organic feedstocks, such as digestates, sewage sludge, woods and other forestry or agricultural residues (Hale *et al.*, 2013; Yao *et al.*, 2012). At present, two main processes are established for the production of chars intended for use in agricultural systems: The more established process is slow pyrolysis, which is the combustion and conversion of biomass at processing temperatures above 450°C under oxygen-free conditions. In the following, we will refer to the solid product derived from pyrolysis as pyrochar. Pyrochars are characterized by a high degree of aromaticity (Keiluweit *et al.*, 2010; Lehmann *et al.*, 2006) and recalcitrance against degradation or mineralization (Glaser *et al.*, 2002). Hydrothermal carbonization (HTC) is a alternative process for char production. HTC implements a low-temperature transformation process (temperatures between 180 and 300°C) combined with high pressure (2-2.5 MPa) and water for several hours (Wiedner *et al.*, 2013; Libra *et al.*, 2011; Funke and Ziegler, 2010). In the following, the solid product from the HTC will be termed hydrochar. Hydrochars have recently received increasing attention since wet feedstock can be carbonized without a drying pretreatment (Funke and Ziegler, 2010). The main characteristics of hydrochars are a lower degree of carbonization and thus more aliphatic carbon (C) and smaller amounts of aromatic C and lower specific surface area (SSA) compared to pyrochars (Eibisch *et al.*, 2013; Titirici *et al.*, 2008). In addition to the general differences between pyrochar and hydrochar, their properties differ

strongly depending on the used feedstock, carbonization process parameters, and subsequent thermo-chemical reactions (Eibisch *et al.*, 2015; Cantrell *et al.*, 2012; Yao *et al.*, 2012; Cao *et al.*, 2011).

The fate of N in soils following the application and decomposition of a variety of materials with high N content such as manure or the organic residuals of household waste (Sánchez-Monedero *et al.*, 2001; Eklind and Kirchmann, 2000), sewage sludge (Malińska *et al.*, 2014; Sánchez-Monedero *et al.*, 2001) or poultry litter (Steiner *et al.*, 2010) has been widely studied. However, only a few studies investigated the effects of char amendment to reduce NH_3 emissions. When ammonium (NH_4^+), urea or uric acid is adsorbed to chars, lower amounts of reactive N can be volatized as NH_3. Spokas *et al.* (2011) showed that chars mixed with slurry can inhibit NH_3 volatilization by surface interactions with NH_4^+ and nitrate (NO_3^-).

Malińska *et al.* (2014) applied 20% woodchips and 5% pyrochars from wood to sewage sludge and found decreased NH_3-emissions of 30-50% within 8 days. The amendment of poultry litter with pyrochars made from pine chips reduced the NH_3 emissions by 64% (80% poultry litter + 20% char) due to NH_4^+ adsorption on pyrochar (Steiner *et al.*, 2010). In contrast, Schimmelpfennig *et al.* (2014) found increased NH_3-volatilization from pig slurry mixed with pyrochars and hydrochars during a 28 h pot experiment. Chars can influence NH_3 emissions either by changing the pH since NH_3 volatilization is pH sensitive or by adsorbing NH_4^+ as precursor of NH_3. NH_3 can also be adsorbed onto the char in the presence of acidic functional groups on the chars' surface or if the char has an acidic pH (Kastner *et al.*, 2009). The study of the adsorption capacity of NO_3^- and NH_4^+ to various activated C and chars showed adsorption onto pyrochars and slight or no adsorption on hydrochars (Gronwald *et al.*, 2015; Ding *et al.*, 2010; Bandosz and Petit, 2009). Studies focusing on soil-char mixtures have shown that leaching of NO_3^-, NH_4^+ from soils amended with pyrochar or hydrochar was frequently reduced by adsorption on the respective char (Bargmann *et al.*, 2014b; Sarkhot *et al.*, 2012; Ding *et al.*, 2010; Laird *et al.*, 2010). However, char effects may be only short term after char application (Gronwald *et al.*, 2015).

However, studies concerning the effect of pyrochar, and especially hydrochar, on soils and manure NH_3 emissions in the temperate zone are rare, and the interaction of different char- manure mixtures is still not understood. Furthermore, no comparison study of the two different char types (pyrochar vs. hydrochar) on reducing NH_3 emissions has been conducted yet. Moreover, most studies were conducted without soil. Thus, the effect of char addition to different types of manure via changes in pH or ammonium adsorption remains unclear. Hence, the objective of this study is to investigate the effect of an admixture of pyrochar and hydrochar produced from the same substrate (*Miscanthus*) to different manure types i.e. cattle slurry (CS) and poultry litter (PL) on NH_3 emissions. We assess chars-induced effect controls NH_3 volatilization in a char-manure mixture: the pH-effect, or the

adsorption of NH_4^+, or both, and determine how surface application of char-manure mixtures to a sandy-loam soil affects dynamics of NH_3 emissions. For this purpose, we conducted a laboratory incubation experiment under controlled conditions. With regard to chars' large SSA and cation exchange capacity (CEC) we hypothesized that adsorption of NH_4^+ will reduce NH_3 volatilization more strongly than the char-induced pH-effect. Consequently, we expected the reduction of NH_3 volatilization to be higher for pyrochar compared to hydrochar treatments.

7.2 Materials and Methods

7.2.1 Production and general properties of pyrochars and hydrochars

Both, hydrochar and pyrochar were produced from *Miscanthus x giganteus*. The pyrochar was produced in a Pyreg reactor by 0.75 h pyrolysis at 750°C. The hydrochar was carbonized with water (1:10, w/w) in a tabular reactor (3 m^{-3}) for 11 h at 2 MPa and 200°C by AddLogicLabs / SmartCarbon (Jettingen, Germany). To catalyze the dehydration process and to increase the C content in the solid product, citric acid powder was added to the *Miscanthus* (Wang *et al.* 2010). All chars were dried at 40°C and sieved ≤ 2 mm. C and N contents were determined via dry combustion (TruSpec, LECO Corp., St. Joseph (MI), USA). Hydrogen and oxygen contents of pyrochars and hydrochars as well as the raw materials were determined with an elementary analyzer (Vario EL3, Elementag, Hanau, Germany). Element contents of chars (e.g. P, Ca, Mg, Na, K, S) of the prepared samples were analyzed using inductively coupled plasma-optical emission spectroscopy (Varian Liberty 150). The pH-value of the chars was determined in 0.01 M $CaCl_2$ with a ratio of 1:5 (volume char / volume solution). Basic characteristics of feedstock, pyrochar, and hydrochar are listed in Table 7.1.

Table 7.1 General properties of feedstock materials and the produced chars.

Feedstock	Char type	Carbonization temperature [°C]	pH ($CaCl_2$)	Ash content [%]	C [%]	N [%]	S [%]	O:C	H:C	P [%]	Ca [%]	Mg [%]	Na [%]	K [%]
Miscanthus	raw	-	-	2.9	46.3	<1.0	<0.1	0.28	0.13	0.09	0.11	0.09	0.01	0.52
	Hydrochar	200	3.8	3.9	63.8	<1.0	<0.1	0.15	0.08	0.13	0.11	0.13	0.21	0.13
	Pyrochar	750	9.0	15.0	81.8	<1.0	0.10	0.09	0.01	0.39	0.35	0.39	0.03	1.50

7.2.2 Soil properties

Soil was sampled from the Ap horizon (0-30 cm) of a Cambic Planosol at a cropland site in the North German lowland in December 2014 (mean annual temperature 8.8°C, around 600 mm precipitation, 52°36'N, 10°89'E, 105 m a.s.l.). The site was managed according to common regional practice with conventional tillage and fertilization. Crop rotation was barley (*Hordeum vulgare*) (2012), mustard (*Sinapis arvensis*) (cover crop), sugar beet (*Beta vulgaris* ssp. *vulgaris*) (2013),

followed by winter wheat (*Triticum aestivum*) (2014). After sampling, the soil was sieved to ≤4 mm and stored for 4 weeks at 4°C until use in the experiment. The soil pH was measured in 0.01 M $CaCl_2$ with a ratio of 1:5 (volume soil : volume solution). C and N contents were determined using dry combustion with an elemental analyzer (TruMac CN, LECO Corp., St. Joseph (MI), USA). Soil texture was determined by the combined sieve and pipette method. The soil has a pH of 6.5 and organic C and total N concentrations of 1.16 % and 0.12 %, respectively (C/N 9.9). The texture is a sandy loam (67.1 % sand, 21.7 % silt, 11.2 % clay).

7.2.3 Manure properties and preparation

CS and PL were used as manure amendments. Four subsamples of 6 L CS were collected and each was mixed to obtain a representative slurry sample. For CS, pH was measured undiluted. CS was stored close in a cold storage room at 4°C. Four 1 kg subsamples of PL were sampled from one manure pit and were mixed afterwards to receive a representative PL sample. Before the pH measurement of PL, we diluted 5 g with 25 g deionized (DI)-water (1:5). PL was also stored close in a cold storage room at 4°C.

Both manures were stirred and pH was measured after 10 min waiting time with a pH combination electrode. Dry matter content was determined gravimetrically after drying the manures at 105°C for 24h in a combustion dryer. Total nitrogen (N_t) was measured on fresh manures using the Kjeldahl method. The NH_4^+ content was determined via distillation and titration using 10 g manure and 50 mL DI-water. The manures' properties can be found in Table 7.2.

Table 7.2 General properties of manures and added manures as applied N to jars in the NH_3 volatilization experiment.

Manure type	pH	Dry matter content [%]	N_t [mg g^{-1}] ± SE (n=4)	NH_4-N [mg g^{-1}] ± SE (n=4)	MFE-N [%]	Applied N per jar [mg N]
Cattle slurry	7.53	10.3	3.14 ± 0.08	1.34 ± 0.01	70	75.6
Poultry litter	8.17	50.4	12.78 ± 1.22	3.39 ± 0.53	80	66.2

We established sub treatments with an addition of acid to the char/manure mixtures in order to differentiate an induced adsorption process of chars from a pH-effect through char addition on NH_3 volatilization. In these treatments, one part of the manures was acidified with sulfuric acid (H_2SO_4) to achieve a pH between 5.5 and 5.8. To avoid a destruction of organic compounds in the manures, 98% sulfuric acid was diluted with DI-water.

7.2.4 NH_3 volatilization experiment

NH_3 measurements & calculations

To determine NH_3 emissions, we used the volatilization-diffusion experimental setup with forced-draft system similar to Rachhpalsingh and Nye (1986) and Roelcke *et al.* (1996). Humidified air (90% relative air humidity) was passed over the soil surface in the jars with an air flow of 16.3 exchange volumes min^{-1} (corresponding to a flow rate of 4.1 L min^{-1} per jar) accordance with Roelcke *et al.* (1996). The air-tight screw cap lids for every jar were designed similar to those of Pacholski *et al.* (2006). Ammonia was trapped as NH_4^+ in a subsequent gas wash flask containing 200 mL of 0.0125 *N* H_3PO_4. In a pre-study it was checked whether emitted NH_3 was completely trapped in the first wash flask. This was done by connecting a second trap to the exhaust air of the first wash flask. Samples from the flask were analyzed for NH_4^+-N using a photometric continuous flow analyzer (SKALAR San++ Continuous-Flow Analyzer, Breda, The Netherlands). The amount of NH_4^+-N in the gas wash flask (N_{GWF}) was calculated as follows:

$$N_{GWF}\,[mg\ N] = [(N_{CGWF} - N_{Blind}) \times V] \qquad \text{(Eq.1)}$$

where N_{CGWF} and N_{Blind} are the determined NH_4^+-N concentration in the gas wash flask and blind vessel [mg L^{-1}]; V is the volume of H_3PO_4 in the gas wash flask [L].

Subsequently, N data from NH_3 volatilization experiment was checked for consistency. For cumulative NH_3-N emissions, inconsistent flux-data due to non-air tight glass jars was deleted and imputed with the mean of remaining replicates.

Experimental design

An incubation experiment under controlled conditions in a climate chamber with 10°C air temperature was conducted during a 4-week period. Overall, a total of 26 treatments were established, each run in quadruplicate (Table 7.3). Additionally to the soil/char/manure/acid treatments, 250 mL blinds (empty jars) were also run in quadruplicate. The treatments without soil were carried out in order to evaluate the influence of the chars on NH_3 volatilization from the manures. Sub-treatments with acid addition to the char/manure mixtures were conducted in order to differentiate an induced adsorption process of chars from a pH-effect through char addition on NH_3 volatilization. Treatments with soil were carried out in order to quantify the effect of either pyrochar or hydrochar on NH_3 volatilization from manure applied to soil. For this purpose, we filled 978 g soil with a bulk density of 1.2 g cm^{-3} in a 1 L glass jar (resulting headspace volume was around 250 mL, soil layer thickness was 20 cm). Subsequently, manure, manure-char, and manure-char-acid mixtures were applied to the soil surface. Manures were applied using mineral fertilizer equivalents (MFE) which indicate the N-use efficiency relative to mineral fertilizer N-use efficiency (UNITO, 2014). According to the corresponding MFE, we wanted to reach an N application rate of 60 kg N

ha^{-1} corresponding to a typical N application rate in maize crops after sowing (April) until July (Wendland and Fischer 2013; LWK-Ni, 2010) via surface application with a trailing hose for CS and even spreading for PL. Trailing hose application covering 0.12 m^2 per 1 m^2 (12%) (hose diameter / -distance = 4 cm / 30 cm) was adapted to our manure application to soil surface in the incubation jars. PL was applied punctually in the center of the soil surface with a diameter of 3 cm.

Table 7.3 Treatment summary and abbreviations.

	Soil	Treatments	Treatment abbreviation
1	without soil	cattle slurry	CS
2		cattle slurry + 10 % (dw/dw) hydrochar	CS+Hydrochar
3		cattle slurry + 10 % (dw/dw) pyrochar	CS+Pyrochar
4		cattle slurry + acid	CS+acid
5		cattle slurry + acid + 10 % (dw/dw) hydrochar	CS+acid+Hydrochar
6		cattle slurry + acid + 10 % (dw/dw) pyrochar	CS+acid+ Pyrochar
7		poultry litter	PL
8		poultry litter + 10 % (dw/dw) hydrochar	PL+Hydrochar
9		poultry litter + 10 % (dw/dw) pyrochar	PL+Pyrochar
10		poultry litter + acid	PL+acid
11		poultry litter + acid + 10 % (dw/dw) hydrochar	PL+acid+Hydrochar
12		poultry litter + acid + 10 % (dw/dw) pyrochar	PL+acid+Pyrochar
13	with soil	soil only	soil
14		Soil + acid	soil+acid
15		cattle slurry + soil	CS+soil
16		cattle slurry + 10 % (dw/dw) hydrochar + soil	CS+Hydrochar+soil
17		cattle slurry + 10 % (dw/dw) pyrochar + soil	CS+Pyrochar+soil
18		cattle slurry + acid + soil	CS+acid+soil
19		cattle slurry + acid + 10 % (dw/dw) hydrochar + soil	CS+acid+Hydrochar+soil
20		cattle slurry + acid + 10 % (dw/dw) pyrochar + soil	CS+acid+Pyrochar+soil
21		poultry litter + soil	PL+soil
22		poultry litter + 10 % (dw/dw) hydrochar + soil	PL+Hydrochar+soil
23		poultry litter + 10 % (dw/dw) pyrochar + soil	PL+Pyrochar+soil
24		poultry litter + acid + soil	PL+acid+soil
25		poultry litter + acid + 10 % (dw/dw) hydrochar + soil	PL+acid+Hydrochar+soil
26		poultry litter + acid + 10 % (dw/dw) pyrochar + soil	PL+acid+Pyrochar+soil

Hence, to reach the N application rate of 60 kg N ha^{-1} and with regard to the soil surface area in the jars (88.25 cm^2), we added 2.41 g (dw) CS (corresponds to 75.6 mg N; ~40% as NH_4^+-N; MFE=70% (LWK-Ni, 2013)) and 2.59 g (dw) PL (corresponds to 66.2 mg N; ~30% as NH_4^+-N; MFE=80% (LWK-Ni, 2013)) per jar, respectively. Char-CS mixtures were produced by either mixing 0.24 g of pyrochar or hydrochar with 2.41 g (dw) CS. With regard to the dry matter content of CS, we added a 25% H_2SO_4 to CS (0.02 mL acid: 1 g fw CS). Char-PL mixtures were produced by either mixing 0.26 g of pyrochar or hydrochar with 2.59 g (dw) PL. The added char amounts correspond to a 10% char addition to manures' dry weight. To improve the mixing process of chars and PL, we added DI-water 1:1 (fw/g water) to the mixture. Regarding to the dry matter contents of PL, we added 12.5% H_2SO_4 to PL (0.25 mL acid : 1 g fw PL : 0.75 mL H_2O). All mixtures were filled into the glass jars and were closed air tight. During incubation, the water content of the soil was controlled by weight and corrected when necessary: at days 3 and 5 we irrigated the surface of all treatments with 2-4 g DI-water to compensate the water loss caused by the strong air exchange.

Soil mineral nitrogen (N_{min})

Soil mineral nitrogen (N_{min} = NO_3^--N + NH_4^+-N) was determined for pure manure and manure-soil as well for acidified and non-acidified treatments after 24 h and 7 d. An additional sample set of manure/char/acid mixtures without soil, similar to that used in the incubation experiment, was set up closed and stored airtight/unventilated for a 24 h at 10°C. Afterwards N_{min} concentrations of manures determined after a 24 h equilibrium period were used as an initial start value. After 7 d, treatments without soil from the volatilization experiment were used to determine the final N_{min} concentration at the end. All samples were extracted by shaking for 1 h to a ratio 1:20 (sample : extracting agent) with 0.01 M $CaCl_2$ to determine N_{min}. After 7 d, manure/char/acid treatments with soil were freshly homogenized. 200 g homogenized soil samples were then extracted with 600 mL 0.01 M $CaCl_2$ by shaking for 1 h. Nitrogen concentrations of the extracts were determined by using photometric continuous flow analyzer (SKALAR San++ Continuous-Flow Analyzer, Breda, The Netherlands). The remaining soil per treatment was used to determine the gravimetric soil water content.

7.2.5 Batch experiments on NH_{4+} sorption kinetics and surface interactions

A sorption equilibrium experiment was conducted to determine the sorption equilibrium of NH_4^+ on chars' surface. The pure manure (control) and manure-char mixtures were filled into 50 mL plastic centrifuge tubes in triplicates. The centrifuge tubes were filled up to 50 mL with DI-water. The tubes were shaken for 24 h at 9 rpm in an overhead shaker. Thereafter, suspensions were centrifuged for 60 min at 4800 × *g* and 4°C. The supernatant was filtered through a fluted paper filter (Grade: 3 hw; Diameter: 150 mm; 65 g m^{-2}) into a 50 mL PE neck bottle. Additionally, to reduce the NH_3 loss during the filtration, the neck bottles were filled with 25 mL 0.01 M H_3PO_4 and the filtration funnels were covered with a paper. Furthermore, the filtration was done in a cold storage room (4°C). The NH_4-concentration in the filtrates was analyzed in the same way as the solutions from the main experiment. Sorbed NH_4^+ in manure-char mixtures was calculated as percentage change in amount of NH_4^+ compared to pure manure as follows:

$$N_{Ads}\,[\%] = \left(\frac{N^1_{Manure} - N^1_{Manure+Char}}{N^0_{Manure}}\right) \times 100, \qquad \text{(Eq.2)}$$

where N^1_{Manure} and $N^1_{Manure+Char}$ are the NH_4^+-N concentrations in pure manure and manure-char mixtures after 24 h shaking time [mg L^{-1}]; N^0_{Manure} is the NH_4^+-N concentration in the pure manure before shaking.

7.2.6 N-Balance calculations

Calculations for the mineral N-balance of treatments without acidification are based on N_{min} values for acidified PL or CS after manure application as amount of N_{min} at the beginning of the experiment assuming that with the addition of acid these start-values imply the highest amount of non-volatized N_{min} from applied N or rather NH_4^+-N (Table 7.4).

Percentage loss of applied NH_4^+-N as NH_3-N was calculated as follows:

$$\%NH_3\text{-}N = \left(\frac{N_{NH3(gas)}}{N_{NH4(manure+acid)}}\right) \times 100, \qquad \text{(Eq. 3)}$$

where $N_{NH3(gas)}$ are the cumulative NH_3-N emissions [mg] from a manure-char treatment and $N_{NH4(manure+acid)}$ is the determined NH_4^+-N concentration [mg] from pure acidified CS or PL.

Without soil, unaccounted N from applied N_{min} was calculated as follows:

$$N_{unacc+nosoil}[mg] = N^0_{\text{min(manure+acid)}} - N^1_{\text{min}(manure-char)} - N_{NH3(gas)}, \qquad \text{(Eq. 4)}$$

where $N^0_{\text{min(manure+acid)}}$ is the amount of total N_{min} of PL+acid or CS+acid at the start of the incubation experiment and $N^1_{\text{min}(manure-char)}$ is the amount of N_{min} of the respective manure-char mixture at the end of the incubation experiment.

With soil, unaccounted N from applied N_{min} was calculated as follows:

$$N_{unacc+soil}[mg] = N^0_{\text{min(manure+acid+soil)}} - N^1_{\text{min}(manure-char)} - N_{NH3(gas)}, \qquad \text{(Eq. 5)}$$

where $N^0_{\text{min(manure+acid+soil)}}$ is the amount of total N_{min} of PL+acid+soil or CS+acid+soil at the start of the incubation experiment and was calculated as follows:

$$N^0_{\text{min(manure+acid+soil)}}[mg] = N^0_{\text{min(soil+acid)}} + N^0_{\text{min(manure+acid)}}, \qquad \text{(Eq. 6)}$$

where $N^0_{\text{min(soil+acid)}}$ is the amount of total N_{min} of incubated acidified soil at the start of the incubation experiment.

7.2.7 Statistical analyses

Statistical analyses were conducted using R 3.1.1 (RCoreTeam, 2014). Since the time course of cumulative NH_3 emissions of non-acidified treatments followed a saturation curve, the asymptotic model

$$F = A \times (1 - e^{-\kappa \times t}), \quad \text{(Eq. 7)}$$

where A [%applied NH_4^+-N] denotes the asymptote of the saturation curve, and κ [1/h] is an exponential decay constant was fit to this data. The fit was done simultaneously to data from all non-acidified treatments using the *gnls* function from R package *nlme* (Pinheiro *et al.*, 2015; Pinheiro and Bates, 2000). This allowed the parameters to be modeled depending on the different treatment factors, i.e., manure type, soil, char type, and acidification. Repeated measures were neglected here, since including random effects precluded successful convergence. However, diagnostic plots indicated that their variance would be very small and they could thus safely be neglected. The resulting analysis of variance (ANOVA) table can be found in Table S1. Table S2 shows the parameters of the fitted asymptotic model including the half-life of the applied NH_4^+-N in the soil-manure system. Temporal dynamics of NH_3 emissions from acidified treatments did not follow an obvious and common model and were therefore not analyzed in this way.

Significance of differences between treatments' cumulated NH_3 emissions were analyzed using ANOVA followed by Tukey's Post-Hoc test ($p < 0.05$). Significance of differences between N_{min} at the start and the end of each treatment in the incubation experiment were tested with Welch's unpaired *t*-test and the resulting *p* values were adjusted for multiple testing using the procedure of Benjamini and Hochberg (1995).

7.3 Results

7.3.1 NH_3 volatilization

NH_3 emissions in treatments without soil

Regarding to NH_3 emissions from pure manures without soil, highest emissions rates were observed within the first hours of the experiment in treatments without acid. A total of 75% of the applied NH_4^+-N from pure PL was lost as NH_3 within 140h (Figures 7.1a & 7.2a).This corresponds to 23% of applied N_t. In the CS treatment, 60% of the NH_4^+-N applied was lost as NH_3 within 140h from pure CS, corresponding to 25% of applied N_t (Figures 7.1b & 7.2e). The modeled half-life of NH_3 emissions from PL and CS without amendments and soil was 10 h and 14 h, respectively (Table S2).

The application of char to the manures affected the NH_3 volatilization: hydrochar reduced it significantly for both manures, while for pyrochar led to slight increases or no change. The reduction of NH_3 volatilization due to hydrochar application was similar for PL and CS with 7% and 10% of the applied NH_4^+-N, corresponding to 3% and 5% of the applied N_t for PL and CS, respectively (Figures 7.1a,b & 7.2a,e). The addition of pyrochar to PL increased the relative NH_4^+-N loss via NH_3 not significantly by 10% (4% of applied N_t) (Figures 7.1a & 7.2a). When applied to CS, pyrochar did not affect the NH_3 volatilization (Figures 7.1b & 7.2g).

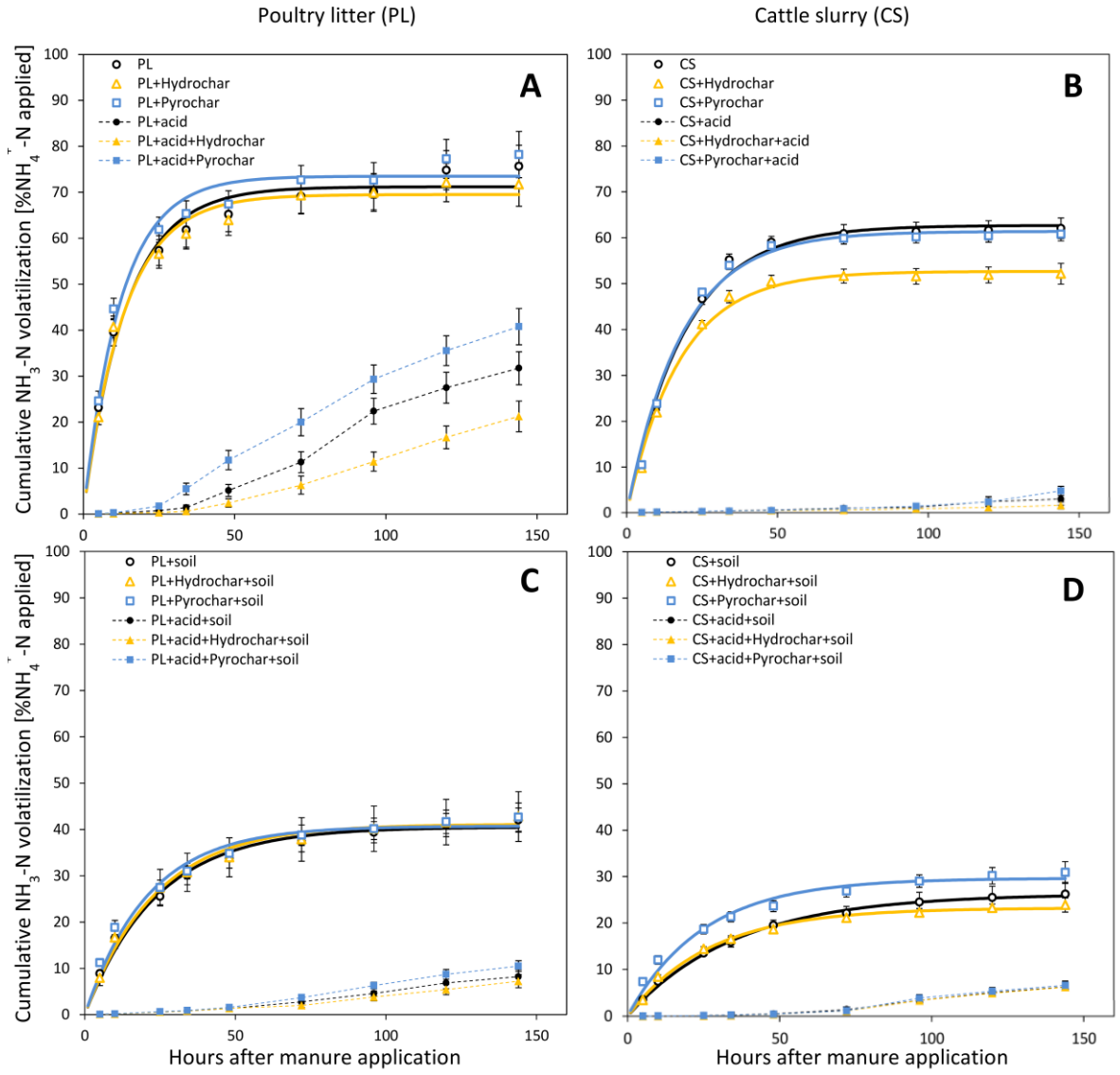

Figure 7.1 Temporal dynamics of cumulative NH_3-N volatilization from manure-char (A, B) and manure-char-soil mixtures (C, D) for poultry litter (PL) and cattle slurry (CS) mixed with pyrochars or hydrochars and with/without acidification as percentage loss as NH_3-N of NH_4^+-N applied during the 7d (140h) incubation experiment. Solid lines indicate modelled NH_3-N volatilization based on the fitted asymptotic model, dashed lines connect measured values for better visualization after cumulating.

Acidification of manure-char mixtures was used to shift the $NH_3(aq)/NH_4^+$-equilibrium towards NH_4^+ to distinguish an additional pH-effect induced by chars from NH_4^+ adsorption due to their corresponding high SSA and CEC. Cumulative NH_3 emissions were lowest in the acidified treatments for both types of manure (Figures 7.1a,b & 7.2b,f). After a lag-time of about 25 h without any NH_3 volatilization, small but continuous NH_3 emission rates (resulting in linear increasing cumulative NH_3-N losses) were observed with acidification for all treatments. Acidification to a pH of 5.5-5.8 reduced total NH_3 emissions by 50% to 70% significantly. After acidification, for PL, significantly lower NH_3 loss (10%) occurred with hydrochar amendment compared to no char addition whereas pyrochar amendment significantly increased NH_3 loss by 10% (Figures 7.1a & 7.2b). In CS treatments without soil, loss as NH_3 was significant higher from amendments with pyrochar than with hydrochar (Figures 7.1b & 7.2f).

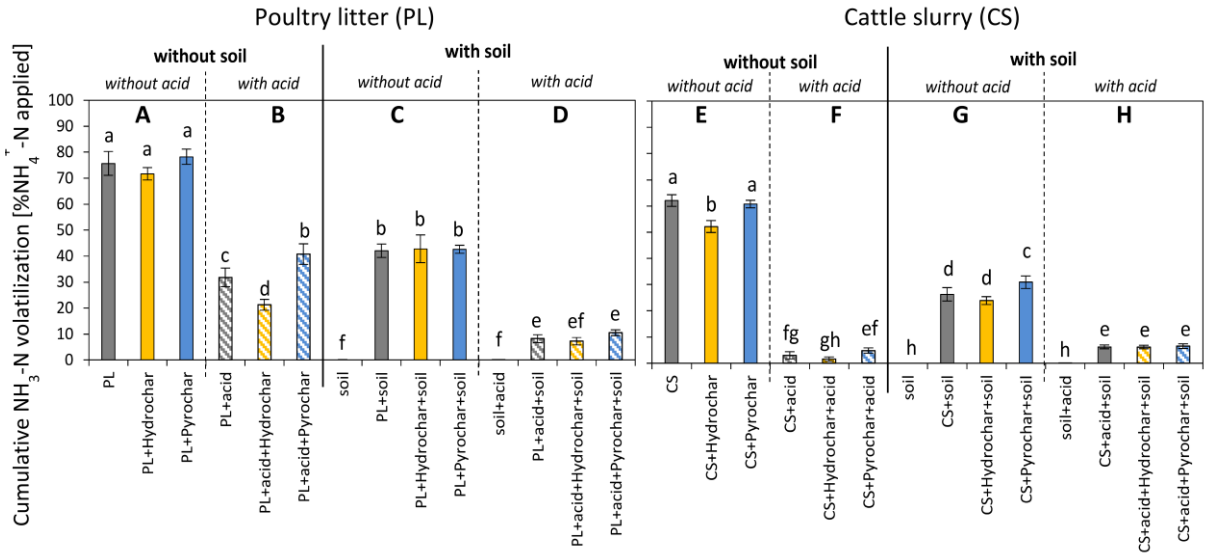

Figure 7.2 Cumulative loss of NH_3-N in percent of NH_4^+-N applied from manure-char (A, B, E, F) and manure-char-soil mixtures (C, D, G, H) for poultry litter (PL)(A-D) and cattle slurry (CS)(E-F) mixed with pyrochars or hydrochars and with/ acidification as percentage loss as NH_3-N of NH_4^+-N applied during the 7d (140h) incubation experiment. Different letters indicate significant differences between treatments within one manure treatment ($p<0.05$, $n=4$).

NH_3 emissions in treatments with soil

In the treatments with manure, char and soil (but without acid), pyrochar addition to CS+soil increased the cumulated NH_3 volatilization significantly by 5 to 8% (2-2.5% of applied N_t) compared to the pure manure mixture without char (Figures 7.1d & 7.2g). The CS+soil amendment with hydrochar reduced the NH_3 volatilization by 2%. In the setup with soil, significantly lower NH_3 emissions occurred with 40% loss from applied NH_4^+-N (10% of applied N_t) from PL and 25% (13% of applied N_t) from CS, which is 25-30% less NH_3 emissions when compared to the treatment without soil (Figures 7.1c,d & 7.2c,g). The modeled half-life of NH_3-emissions was 17 h and 23 h for PL and CS, respectively (Table S2).

When acid was added to the manure+char+soil mixtures, no significant differences were observed between the two manure treatments. Cumulative NH_3-N emissions continued to increase slightly after manure application until the end of the experiment in the treatments with the addition of acid. During this period, we observed constant low emission rates at every sampling time.

7.3.2 Batch experiments on NH_4^+ sorption

The amount of NH_4^+-N in the manure composites refers to the amount of NH_4^+ in pure manures as percentage change of NH_4^+-N applied. Negative (positive) values indicate a decrease (increase) of NH_4^+ in the batch solution, respectively. In the treatments without acid, the amount of NH_4^+ was significantly reduced by 20% in the batch solution from PL+Pyrochar (Figure 7.3a). When PL was mixed with hydrochar, the amount of NH_4^+ in the batch solution was reduced not significantly by 5%. For CS, addition of char has no effect on the amount of NH_4^+ in the batch solution (Figure 7.3c).. With acidification, while the amount of NH_4^+ in pure PL was significantly reduced by 17%, acidification has no influence on the NH_4^+ amount in pure CS. The addition of pyrochars to PL+acid increased the amount of NH_4^+ not significantly by 7% (Figure 7.3b). When applied to PL+acid, hydrochars has no effect on NH_4^+ in the batch solution. In all CS+acid treatments, the addition of chars did not significantly affect the amount of NH_4^+ in the batch solution (Figure 7.3d).

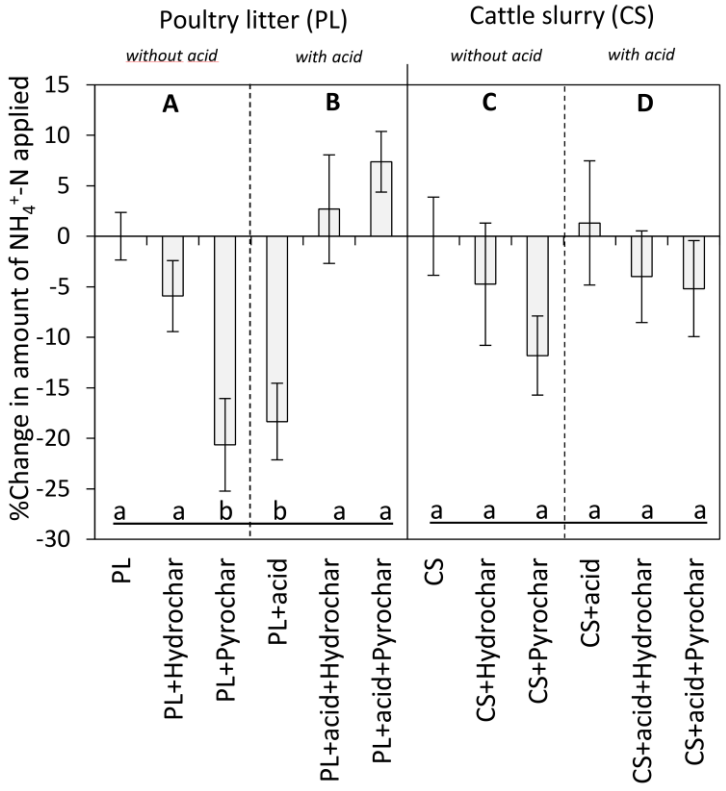

Figure 7.3 Relative changes of NH_4^+-N in the manure-char (A & C) and manure-char-acid (B & D) composites for poultry litter (PL) and cattle slurry (CS) mixed with pyrochars or hydrochars as residual percentage of NH_4^+-N applied after 24 h shaking in the batch sorption-kinetic experiments. Means and standard errors (n=3). Different letters indicate significant differences within same manure treatment ($p<0.05$).

7.3.3 N-balance

Net nitrification and ammonification processes were investigated by determining the concentrations of NH_4^+-N and NO_3^--N in the manure-amended soil. An increase in NH_4^+ concentrations represents positive net ammonification whereby an increase in NO_3^- concentration represents net nitrification. Under the presence of soil, when significant different from zero unaccounted N from applied N_{min} indicates unexplained N loss. Without soil, absolute cumulative NH_3-N emissions indicate a volatilization of N_{min} from both manures due to a significant decrease of the NH_4^+ pool from the start to the end of the incubation experiment (Table 7.4).

For treatments without acid, around 75% of the applied N_{min} from PL and around 60% from CS were lost as NH_3. While the addition of pyrochar to both manures did not affect the amount of N_{min}, hydrochar addition to CS resulted in significant higher amounts of N_{min} (12.6±0.5 mg) at the end of the incubation experiment due to lower NH_4^+ volatilization compared to pure CS (9.2±0.4 mg) and CS+Pyrochar (9.1±1.9 mg).

N_{min} was less volatilized with acidified manures resulting in higher amounts of NH_4^+ in the pure manures (CS+acid: 28.3±1.4 mg; PL+acid: 13.4±0.9 mg) or manure-char mixtures compared to non- acidified treatments (CS: 9.2±0.4 mg; PL: 2.6±0.1 mg) after seven days. In CS+acid and CS+acid+Hydrochar treatments, total amount of NH_4^+ did not change significantly over the incubation time resulting in cumulative absolute NH_3 emissions around zero. For the N-balance calculations without soil, unexplained unaccounted N from applied N_{min} was not significantly different from zero.

Due to the addition of soil, higher amounts of NO_3^--N were in the soil-manure systems which increased significantly from start to the end of the experiment. For both manure treatments, the amount of NO_3^--N increased from 11.2±0.5 to 16.2±0.7 mg for PL and from 11.1±0.5 to 25.8±0.8 mg for CS. The addition of chars to manure+soil treatments did not affect the amounts of NO_3^-. With acidification, the amount of NO_3^--N increased to 15.6±0.6 and 22.1±0.8 mg for PL and CS, respectively. The addition of chars has no effect on NO_3^- for either manures. Non-recovered N from applied N_{min} was significant different from zero (p<0.05) for seven out of twelve cases for manure treatments with soil and/or acidification of manure and soil.

Table 7.4 Mean N_{min} (NH_4^+-N + NO_3^-- N) derived from applied N per glass jar as well as cumulative NH_3-N loss and calculated unaccounted N from applied NH_4^+-N (Means and (standard error), n=4). Different lower case letters indicate significant differences within one manure treatment ($p<0.05$, n=4). Different capital letters indicate significant differences between start and the end of the experiment. *P*-value indicates if unaccounted N is significant different to zero (*$p<0.05$).

Treatment	After manure application (start)						7 days after manure application (end)						Cumulative NH_3-N emissions [mg] (SE)		%NH_3-N loss from applied NH_4-N (SE)		Unaccounted N from applied Nmin [mg] (SE)	
	N_{min} [mg] (SE)		NH_4^+-N fraction [mg] (SE)		NO_3^--N fraction [mg] (SE)		N_{min} [mg] (SE)		NH_4^+-N fraction [mg] (SE)		NO_3^--N fraction [mg] (SE)							
Without acid / without soil																		
PL	**12.5 a**	(0.4)	12.5	(0.9)	0.0	(0.0)	**2.6 aB**	(0.1)	2.6	(0.3)	0.0	(0.0)	**15.0 a**	(1.5)	**75.6 a**	(4.6)	**-1.0**	(2.0)
PL+Hydrochar	**13.0 a**	(0.4)	13.0	(0.9)	0.0	(0.0)	**2.2 aB**	(0.2)	2.2	(0.3)	0.0	(0.0)	**14.2 a**	(0.8)	**71.7 a**	(2.4)	**0.6**	(1.7)
PL+Pyrochar	**13.2 a**	(0.6)	13.2	(1.1)	0.0	(0.0)	**2.8 aB**	(0.6)	2.8	(1.3)	0.0	(0.0)	**15.5 a**	(0.9)	**78.2 a**	(2.9)	**-2.1**	(2.0)
CS	**22.1 a**	(2.3)	22.1	(4.6)	0.0	(0.0)	**9.2 aB**	(0.4)	9.2	(0.4)	0.0	(0.0)	**18.8 a**	(0.5)	**62.1 a**	(2.3)	**0.8**	(2.8)
CS+Hydrochar	**23.1 a**	(0.6)	23.1	(1.2)	0.0	(0.0)	**12.6 bB**	(0.5)	12.6	(0.5)	0.0	(0.0)	**15.8 b**	(0.3)	**52.1 b**	(2.3)	**0.5**	(3.9)
CS+Pyrochar	**22.5 a**	(2.0)	22.5	(3.9)	0.0	(0.0)	**9.1 aB**	(1.9)	9.1	(1.9)	0.0	(0.0)	**18.4 a**	(0.5)	**60.8 a**	(1.4)	**0.4**	(4.2)
With acid / without soil																		
PL+acid	**19.9 aA**	(0.4)	19.9	(0.8)	0.0	(0.0)	**13.4 aB**	(0.9)	13.4	(1.8)	0.0	(0.0)	**6.3 a**	(1.2)	**31.7 a**	(3.6)	**0.0**	(2.5)
PL+acid+Hydrochar	**20.1 aA**	(0.7)	20.1	(1.5)	0.0	(0.0)	**15.9 aB**	(0.5)	15.9	(0.9)	0.0	(0.0)	**4.2 b**	(0.7)	**21.3 b**	(2.1)	**-0.1**	(1.9)
PL+acid+Pyrochar	**19.3 aA**	(0.4)	19.3	(0.8)	0.0	(0.0)	**11.1 aB**	(0.3)	11.1	(0.6)	0.0	(0.0)	**8.1 c**	(1.3)	**40.8 c**	(3.9)	**-1.9**	(2.0)
CS+acid	**30.2 aA**	(1.8)	30.2	(3.6)	0.0	(0.0)	**28.3 aA**	(1.4)	28.3	(2.9)	0.0	(0.0)	**0.9 a**	(0.7)	**3.0 a**	(1.4)	**-0.4**	(3.9)
CS+acid+Hydrochar	**30.3 aA**	(3.2)	30.3	(6.3)	0.0	(0.0)	**29.5 aA**	(0.7)	28.5	(1.4)	0.0	(0.0)	**0.5 a**	(0.4)	**1.6 a**	(0.8)	**-0.1**	(4.3)
CS+acid+Pyrochar	**30.2 aA**	(1.9)	30.2	(3.7)	0.0	(0.0)	**28.3 aB**	(0.4)	26.3	(0.8)	0.0	(0.0)	**1.5 b**	(0.5)	**4.8 b**	(1.0)	**0.1**	(2.8)
Without acid / with soil																		
soil	**12.5**	(0.3)	0.1	(0.0)	12.4	(0.6)	**12.5**	(0.3)	0.1	(0.0)	12.4	(0.6)	-	-	-	-	**-0.2**	(0.6)
PL+soil	**32.5**	(1.2)	20.0	(0.6)	12.5	(0.6)	**19.0 aB**	(0.4)	2.7 aB	(0.2)	16.2 aB	(0.7)	**8.3 a**	(0.9)	**42.0 a**	(2.6)	**3.9**	(1.6)
PL+Hydrochar+soil							**16.9 bB**	(0.3)	2.6 abB	(0.1)	14.3 bB	(0.5)	**8.5 a**	(1.7)	**42.8 a**	(5.4)	**5.8**	(2.4)
PL+Pyrochar+soil							**18.8 aB**	(0.3)	2.3 bB	(0.2)	16.5 aB	(0.4)	**8.5 a**	(0.5)	**42.6 a**	(1.5)	**4.0***	(1.2)
CS+soil	**42.8**	(1.2)	30.3	(0.6)	12.5	(0.6)	**28.3 aB**	(0.6)	2.5 aB	(0.4)	25.8 aB	(0.8)	**7.9 a**	(0.2)	**26.2 a**	(2.6)	**5.2***	(1.3)
CS+Hydrochar+soil							**28.1 aB**	(0.8)	3.4 bB	(0.1)	24.8 aB	(1.5)	**7.2 a**	(0.2)	**23.9 a**	(1.5)	**6.1***	(1.5)
CS+Pyrochar+soil							**28.3 aB**	(0.7)	1.9 cB	(0.1)	26.3 aB	(1.3)	**9.3 b**	(0.4)	**30.9 b**	(2.4)	**3.8**	(1.6)
With acid / with soil																		
soil+acid	**11.3**	(0.3)	0.1	(0.0)	11.1	(0.5)	**11.3**	(0.3)	0.1	(0.0)	11.1	(0.5)	-	-	-	-	**-0.0**	(0.6)
PL+acid+soil	**31.2 A**	(1.0)	20.0 A	(0.5)	11.2 A	(0.5)	**24.3 aB**	(0.6)	8.7 aB	(0.6)	15.6 aB	(0.6)	**1.6 a**	(0.5)	**8.2 a**	(1.6)	**5.3***	(1.6)
PL+acid+Hydrochar+soil							**24.1 aB**	(1.1)	9.7 aB	(1.6)	14.5 aB	(0.6)	**1.4 a**	(0.5)	**7.3 a**	(1.4)	**5.6***	(2.1)
PL+acid+Pyrochar+soil							**23.9 aB**	(1.0)	8.6 aB	(1.0)	15.3 aB	(0.9)	**2.1 b**	(0.4)	**10.5 b**	(1.1)	**5.2***	(1.9)
CS+acid+soil	**41.4 A**	(1.0)	30.3 A	(0.5)	11.2 A	(0.5)	**33.9 aB**	(1.5)	11.9 aB	(2.3)	22.1 aB	(0.8)	**1.9 a**	(0.3)	**6.2 a**	(0.7)	**5.6**	(3.3)
CS+acid+Hydrochar+soil							**34.3 aB**	(1.1)	12.7 aB	(1.0)	21.6 aB	(1.1)	**1.9 a**	(0.3)	**6.2 a**	(0.7)	**5.3**	(2.8)
CS+acid+Pyrochar+soil							**33.1 aB**	(0.7)	11.8 aB	(0.5)	21.3 aB	(0.8)	**2.0 a**	(0.4)	**6.6 a**	(0.9)	**6.3***	(2.5)

7.4 Discussion

7.4.1 Influence of char amendment of manure on NH_3 emissions

Hydrochar addition led to reduced NH_3 volatilization for both investigated manures due to its acidic pH (3.8) which implicates a stronger reduction-effect on manures' pH with our used hydrochars by shifting the $NH_3(aq)/NH_4^+$-equilibrium towards NH_4^+. The conversion of aqueous NH_4^+ to volatilizable NH_3 is pH-dependent starting at around pH 6.5 ($NH_3(aq)/NH_4^+$ ratio: 0.01) (Bates and Pinching, 1950). Schimmelpfennig *et al.* (2014) also reported significant lower NH_3 emissions from pig slurry amended with hydrochar from *Miscanthus* compared to pyrochar addition. This is due to hydrochars' low pH (5.1) or the microbial N immobilizing capacity as reported by Gajić and Koch (2012). The authors suggest a remineralization of previously immobilized N through hydrochar addition with a low C/N ratio. Furthermore, the physicochemical properties of hydrochar result in a lower stability against microbial degradation. Therefore, hydrochars provides high amounts of easily degradable C to microorganisms which promote microbial-biomass production. Thus it has been suggested that N immobilization as well as a higher nitrification from NH_4^+ to NO_3^- may occur (Bargmann *et al.*, 2014a; Lehmann *et al.*, 2011). However, we cannot verify this assumption, because no increased amount of NO_3^- was observed in manures.

The addition of pyrochars to both manures led to increase NH_3 emissions or showed no significant effect compared to pure manures. The affected NH_4^+-N loss as NH_3 due to pyrochar mixing with slurry manure was not significant, which is in accordance with findings by Taghizadeh-Toosi *et al.* (2011) who reported 1.4% lower NH_3 losses of the applied N due to pyrochar from woodchip addition to cow urine. Enhanced NH_3 emissions were observed by Schimmelpfennig *et al.* (2014) with 12% loss of the applied NH_4^+ fraction from pig slurry. On the other hand, the higher N loss as NH_3 due to PL amendment with pyrochar compared to pure PL was contrary to observations reported by Doydora *et al.* (2011) and Steiner *et al.* (2010), who found a 58 to 64% reduction of NH_3 emissions after pyrochar addition to PL. One likely reason for the observed reduction in NH_3 emissions in the study by Doydora *et al.* (2011) is that the applied char was acidified and therefore acted as acid carrier which strongly reduced the $NH_3(aq)/NH_4^+$-equilibrium towards NH_4^+, which may directly adsorbed to pyrochars surface. We assume that with their high pH (mostly above pH 8) the liming effect of pyrochars competes with their adsorptive properties on NH_4^+. For manures, we suggest an imbalanced ratio between liming and adsorption towards stronger liming of manures, which results in a slight shift of the $NH_3(aq)/NH_4^+$-equilibrium towards NH_3. Further, in these two studies, the char application rate was markedly higher than in our experimental setup: Doydora *et al.* (2011) added 1:1 (dw/dw) acidified pyrochars from pine chips and peanut hulls and Steiner *et al.* (2010) even used 95% PL + 5% pyrochar and 80% PL + 20% pyrochar mixtures. These

considerably higher applications compared to our study (1:10 dw/dw), resulted in a markedly higher specific surface area available for NH_4^+ sorption, which may in turn be responsible for the reduction of NH_3 emissions observed in those studies. Last but not least, the pyrochar in our study was i) produced at higher carbonization temperature (950 vs. 400°C) and ii) converted from beech-woodchips instead of pine-woodchips. A variety of studies emphasize that major properties (e.g. SSA, CEC, ash content) of chars are affected by feedstock, carbonization process parameters, and subsequent thermochemical reactions (Eibisch *et al.,* 2015; Eibisch *et al.,* 2013; Cantrell *et al.,* 2012; Yao *et al.,* 2012; Cao *et al.,* 2011). With regard to our findings, we suggest that for our used pyrochars the liming effect to manures was stronger than the potential NH_4^+ adsorption.

7.4.2 Influence of manure acidification on NH_3 emissions

Acidification to a pH of 5.5-5.8 reduced total NH_3 emissions by 50% to 70% which is in the range reported by Kai *et al.* (2008) (50-70%) and Petersen *et al.* (2012) (95% after acidifying CS to pH 5.5). Furthermore, we observed slight but continuously low NH_3 emission rates from acidified treatments after a 25 h lag-time. Dai and Blanes-Vidal (2013) also found constant low NH_3 emissions for a period of time related to the pH of acidified pig slurry. The authors reported a tenfold prolonged lag time by changing the slurry pH from 6.0 to 5.5. We assume that in the first 24 h hours i) the addition of acid shifted the NH_3(aq)/NH_4^+-equilibrium towards 100% NH_4^+ (pH: 5.5) which significantly suppressed the NH_3-volatilization and afterwards ii) the acidity decreased by slight consumption of H^+ through urease which increased during urea hydrolysis to NH_3. Especially PL contains uric acid, which can be converted to urea by the enzyme uricase, and is in turn hydrolyzed to NH_3-N by the enzyme urease, thereby consuming H^+ ions and increasing pH during the process (Ferguson *et al.,* 1984). However, especially for both acidified manure treatments, the duration of the volatilization experiment was too short (140 h) to be able to draw any assumptions about further NH_3 emissions. Dai and Blanes-Vidal (2013) reported low but slight increasing NH_3 emission rates over a period of 264 h which equalize to emission rates compared to without acidification. Therefore, we think that the duration of the experiment was sufficient, because it covered the lag-time in NH_3 emissions. It is recommended that manures have to be incorporated into soils immediately after application (Webb *et al.,* 2010) which could be performed during the lag-time. When non-acidified slurry is immediately incorporated into soils, NH_3 emissions can be reduce by 90-99% (Thompson and Meisinger, 2002). Incorporation of slurry 3 to 6 h after application reduced NH_3 emissions by 60% (Webb *et al.,* 2010). NH_3 emissions from solid manure can be reduce by a range of 80-92% (McGinn and Sommer, 2007; Webb *et al.,* 2004) when immediately incorporated into soils. When solid manures were incorporated into soil 4 h after application, NH_3 emissions can reduce by 70-90% (Rodhe and Karlsson, 2002; Sagoo *et al.,* 2007). Furthermore, we found nitrification of NH_4^+ to NO_3^- in acidified manure+soil treatments.

Furthermore, during manure acidification, we observed significant bubble formation in both manure types. As proposed by Petersen *et al.* (2012) we assume that this is an accumulation of CO_2 in the slurry which may additionally lower the pH below the targeted pH-value. This could result in a slight lower pH-value of manures in the first hours of the experiment than measured initially.

7.4.3 Influence of soil-presence on NH_3 emissions

The presence of soil lowered the total NH_3 loss significantly, probably due to manure infiltration into the pore space and subsequently through several possible processes which reduce the amount of NH_4^+ as preliminary stage of NH_3 from manure: i) NH_4^+ from manure could be immobilize into soil organic matter (SOM), ii) due to NH_4^+- adsorption/(fixation) on (clay) minerals surfaces, iii) oxidation of the NH_4^+-pool to NO_2^- and NO_3^- by nitrification and iv) by gaseous N losses as N_2O from nitrification or N_2O and N_2 from denitrification coupled to nitrification (Wrage *et al.*, 2001). Our findings show significant amounts of unaccounted N after manure application in 7 of 12 treatments with soil. When significant different from zero, unaccounted N indicates N loss via immobilization or gaseous loss as N_2O and/or N_2. We found significant higher amounts of NO_3^- in treatments with soil after manure application. This promotes the assumption that nitrifying/denitrifying microorganisms converted additionally NH_4^+ from manures into NO_3^- (and gaseous N_2O or N_2). Furthermore, nitrification was higher for CS+soil treatments compared to PL+soil treatments. For non-acidified treatments, we assume for CS+soil and CS+Hydrochar+soil that i) the largest proportion from the NH_4^+-pool was nitrified into NO_3^- and ii) a smaller proportion was lost as gaseous N_2O and/or N_2 emissions. For acidified treatments, higher amounts of NH_4^+ were infiltrating into the soils' pore space followed by adsorption/fixation on (clay) mineral surfaces. Another mechanism to reduce NH_3 emissions by soil are interactions between reduced urea hydrolysis through the presence of calcium carbonate ($CaCO_3$) in soil resulting in a pH depression (Fenn *et al.*, 1981). Our used soil has a pH of 6.5 as indicator for the presence of $CaCO_3$ which may verify this assumption. In summaty, we assume that infiltration of manures into poor space and subsequently adsorption on mineral surfaces and nitrification were the main factors which reduced NH_3 emissions driven by soil presence. The proportion of nitrification/denitrification of NH_4^+ to N_2O and N_2 were also possible but not measured.

7.4.4 NH_4^+ sorption and surface interactions (batch experiments)

Our observations showed no NH_4^+ adsorption by the used chars. Hence our results point out that the effects of char addition to manure on NH_3-emissions were almost exclusively driven by the char´s effect on pH. This is in accordance with findings by Mumme *et al.* (2014). They mixed 2 g pyro- and hydrochars with a biogas inoculum mixture of cattle slurry, maize and maize silage in a batch fermentation experiment and found that the alkalinity of the used pyrochar with a pH of 9.0 shifted

the NH_3-NH_4^+ dissociation equilibrium towards NH_3, resulting in lower amounts of NH_4^+ and higher NH_3 emissions. In contrast, the acidity of hydrochars with a pH of 3.8 could shift the dissociation equilibrium towards NH_4^+ resulting in less NH_3 emissions. On the other hand, our findings are not in line with previous studies which showed adsorption of NH_4^+ from nutrient solutions with soil-pyrochars mixtures and no or marginal adsorption by soil-hydrochars mixtures from batch experiments (Gronwald *et al.,* 2015; Hale *et al.,* 2013; Sarkhot *et al.,* 2013; Yao *et al.,* 2012). For the tested chars, this suggests that the ability of chars to decrease N losses via NH_3 volatilization through adsorption is minor when the chars are applied directly to manure. Another char surface mechanism to decrease NH_3 volatilization by chars is described by Seredych and Bandosz (2007) and Seredych *et al.* (2009), and is discussed in Spokas *et al.* (2011). The authors suggest that under ambient conditions, NH_3 can act as a Brownsted and/or Lewis acid. This leads to the formation of an NH_4-salt or an amide following reaction with acidic carboxyl groups on chars' surface. Furthermore, water can compete with NH_3 for binding sites, whereas water films on chars' surface increase the dissolution of NH_3 into the water film, creating NH_4^+ (Seredych and Bandosz, 2007; Seredych *et al.,* 2009). But in this experiment no increase of NH_4^+ in the batch solution was found.

7.5 Conclusion

The effect of pyrochar and hydrochar produced from *Miscanthus* on NH_3 emissions from organic manure was mainly driven by char-induced pH changes. A reduction of NH_3 emissions due to adsorption of NH_4^+ especially to pyrochar was not observed. However, pH management of manure by char addition to reduce NH_3 emissions is rather ineffective as compared to direct acidification. However, when acidification is used the lag time (25 h) in NH_3 volatilization must be used as time frame to incorporate organic manures into soil. To reach the same NH_3 reduction potential as acidification, a large, and therefore expensive, amount of char would be required. When char is added to acidified manures, the chars' contribution towards reducing NH_3 volatilization from manure was 10% of applied NH_4^+-N (up to 5% of the applied N_t). Therefore, based on our methods and observations, we do not recommend the use of char to reduce NH_3 volatilization from organic manure.

7.6 References

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CHAPTER 8 STABILITY OF PYROCHAR AND HYDROCHAR IN DIFFERENT AGRICULTURAL SOILS - A NEW FIELD INCUBATION METHOD

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Abstract

The application of chars on soils offers an option to sequester carbon (C) and to improve soils' fertility. Different types of chars are available as soil amendments, produced with two different processes: pyrochar produced with pyrolysis and hydrochar produced with hydrothermal carbonization. However, there is no study to assess the stability of these two char types in soils *in situ* at field sites. With the newly developed mini-plot methods we were able to assess the decomposition dynamic of chars with few operational costs. Zinc was used as inert tracer mixed with the char in order to be able to correct for mixing of surrounding soil material into the mini-plots, e.g. due to tillage. We used *Miscanthus* (C4-plant) as feedstock with higher ^{13}C concentration than the soil C. The difference in ^{13}C abundance allowed the calculations of char-derived C in the soil at three sampling dates. While C derived from pyrochar did not change over time, hydrochar-C decreased 75±20% after 19 months *in-situ* field incubation. There was no difference in the decomposition dynamics of the chars among the three field sites with different soil types. Moreover, we did not observe a decline in decomposition rates with time but the data were well fitted with a linear one-pool decay model. The model derived mean residence times were 5±1 years for hydrochar and (with larger uncertainty) 42±10 years for pyrochar. Thus, while pyrochar has a high potential for C-sequestration, faster mineralization of hydrochar compared to pyrochar showed their potential to act as a long-term fertilizer through slow nutrient release to soils.

8.1 Introduction

Intensive land use and current agricultural practices have led to the degradation of soil and to decreasing content of soil organic matter (SOM) (Lal and Bruce, 1999; Lal and Kimble, 1997; Paustian *et al.*, 1997). New technologies are required to capture atmospheric C and store it stabilized in soils to counteract the increased accumulation of C in the atmosphere as CO_2 and to counteract soil C loss. In the past ten years, the long term storage of atmospheric C in the soil to mitigate global warming has gained increasing attention. The application of char to agricultural soils could be an option to mitigate climate change by fixing atmospheric C. Besides the ability to sequester soil-C, several positive co-benefits are attributed to char when it is mixed into agricultural soils: increasing yields due to the retention of plant available nutrients in the rhizosphere (Lehmann and Joseph 2009) as a result of increased soil pH and soil cation exchange capacity (CEC) (Liang *et al.*, 2006); enhanced soil water holding capacity (Abel *et al.*, 2013; Glaser *et al.*, 2002); decreasing greenhouse gas emissions of nitrous oxide (N_2O) and methane (CH_4) as well as the preservation of toxic compounds such as heavy metals (Chen and Yuan, 2011). Carbon from crop residuals, such as from maize, can be mineralized by up to 75% within one year and the mean residence time (MRT) for maize-C in soils ranges from 5 to 7 years (Li *et al.*, 2016; Ajwa and Tabatabai, 1994;). *Miscanthus* as feedstock to produce chars received rising attention as a potential bioenergy crop (Clifton-Brown *et al.*, 2007; Heaton *et al.*, 2004). Besides producing substitutes for fossil fuels, *Miscanthus* can increase SOM by the large belowground biomass, as well as from dead below- and aboveground biomass which has been incorporated into the soil (Poeplau and Don, 2014). However, amendment of soil with chars has the advantage that it is much more recalcitrant against mineralization than its original feedstock. For example, *Miscanthus*-derived C in SOM has an MRT of between 1.0 and 3.5 years (Foereid *et al.*, 2004) compared to the range of 40 to 4000 years when converted into e.g. pyrochar (Fang *et al.*, 2014; Kuzyakov *et al.*, 2014; Hamer *et al.*, 2004;).

Chars are the solid charcoal product gained from the thermal transformation of biomass, such as woods and other agricultural or forestry residues, digestates, and sewage sludge (Hale *et al.*, 2013; Lehmann and Joseph 2009). Currently, two main processes are used for the production of char intended for use in agricultural systems: i) Slow pyrolysis, which is the combustion and conversion of biomass at processing temperatures above 450°C under oxygen-free conditions. ii) Hydrothermal carbonization (HTC), which is a low-temperature transformation process (temperatures between 180 and 300°C) in the presence of water and high pressure (2.0-2.5 MPa) for several hours (Wiedner *et al.*, 2013; Libra *et al.*, 2011; Funke and Ziegler 2010; Yu *et al.*, 2004). In the following, we term the solid product derived from pyrolysis “pyrochar”. Pyrochars are characterized by a high recalcitrance against degradation or mineralization (Glaser *et al.*, 2002) and a high degree of aromaticity (Keiluweit *et al.*, 2010; Lehmann *et al.*, 2006). And we will refer to the solid product

from the HTC as hydrochar. Hydrochars have recently received increasing attention since wet feedstock can be carbonized without the pretreatment of drying (Funke and Ziegler, 2010). The main characteristics of hydrochars are a lower specific surface area (SSA) compared to pyrochars (Eibisch *et al.,* 2013; Titirici *et al.,* 2008) and a lower degree of carbonization and thus more aliphatic carbon (C) but less aromatic C as compared to pyrochar. Furthermore, hydrochars have higher H:C and O:C ratios, which mean that they have higher amounts of plant-derived surface functional groups on the chars' surface (Schimmelpfennig and Glaser, 2012). In addition to the general differences between pyrochar and hydrochar, their properties strongly depend on the carbonized feedstock, the thermo-chemical reactions during charring, and carbonization process parameters (Eibisch *et al.,* 2015; Cantrell *et al.,* 2012;Yao *et al.,* 2012; Cao *et al.,* 2011).

Climatic conditions, water content, soil type, the initial SOM content of the soil and the nutrient availability is determining for soil microbial activity and thus C mineralization (Lu *et al.,* 2014; Zimmerman *et al.,* 2011). Abiotic and biotic processes can degrade char and thus change its properties e.g. sorption behavior (Gronwald *et al.,* 2015; Liu *et al.,* 2013; Hale *et al.,* 2011; Steinbeiss *et al.,* 2009; Cheng *et al.,* 2008). Abiotic processes in soils affect the labile C fraction decomposition rate as well as the short-term char oxidization, which is indicated by a decrease in pH, as well as an increase in cation exchange capacity (CEC) and oxygen (O) content (Cheng *et al.* 2006). Cheng *et al.* (2006) suggested that the formation of carboxylic functional groups is the reason for enhanced CEC during oxidation. For effective soil amendment, char degradation is more relevant than C sequestration because nutrients that are incorporated into chars can be released (Abiven *et al.,* 2011). Over time, slow char aging due to oxidization may produce carboxylic and phenolic functional groups. On the other hand, the atomic C content and surface positive charge on the edge sites of aromatic compounds will be reduced (Cheng *et al.,* 2008; Cheng *et al.,* 2006; Glaser *et al.,* 2000). With regard to the specific use, there is competition between the stability and functionality of chars. The more stable the chars are, the lower their functionality due to decreasing functional groups on chars' surface (Schimmelpfennig and Glaser, 2012). However, in order to evaluate chars' potential as an agricultural amendment and as an option to mitigate climate change, it is necessary to know their stability against mineralization once they are applied to soils.

Laboratory incubation studies were generally used to assess the C-mineralization dynamics of char-amended soils, and first long term experiments in the laboratory suggest a high persistence of pyrochar against mineralization (Kuzyakov *et al.,* 2014). Gajić *et al.* (2012) applied 30 Mg char ha^{-1} pyrochars and hydrochars from sugar beet pulp to Cambisol-derived soil samples in an 8-month laboratory incubation experiment and reported a mineralization of hydrochars and pyrochar of 12 to 32%, and 3%, respectively. Lu *et al.* (2014) applied 0.5% (dw/dw) pyrochars from corn straw to samples from an aquic Inceptisol, which is equivalent to an application rate of 15 Mg ha^{-1}. Samples

were incubated with and without additional N in a 30-day laboratory incubation experiment. Without N amendment, the authors did not observe any char mineralization. The mineralization of native SOC was reduced by 65-69% with the addition of N. The authors assumed that the combination of inhibited decomposition due to char addition and the stimulation by inorganic N on native SOC mineralization caused a negative priming effect. Bamminger *et al.* (2014) incubated 16 and 32 Mg ha^{-1} pyrochar and hydrochar from maize silage for 57 days in a laboratory experiment with one forest and one arable soil. They reported that 13-16% of the added hydrochar was mineralized within 8 weeks. They also observed that with the addition of hydrochar, the mineralization of SOC was stimulated by inducing positive priming effects. Pyrochars' mineralization was between 1 and 3% and comparable to the SOC in control soil.

All studies agree that chars can be mineralized, but the rates are different depending on environmental conditions (Zhao *et al.*, 2015) and the quality of the char. However, most studies on the stability of char are too short to deduce data on mid and long-term char stability and are conducted as incubation studies in the laboratory, where environmental controlling factors on char stability are ignored. No systematic comparison of the recalcitrance of pyrochars and hydrochars from the same feedstock has yet been conducted in a long term field experiment. Many studies, however, are still conducted in a laboratory setting with often unknown bias in results and limited transferability into the "real world". Furthermore, there is a large discrepancy between decomposition rates and MRTs estimated from incubation studies showing slower char-C mineralization and life-times of millennia (Bamminger *et al.*, 2014; Fang *et al.*, 2014; Kuzyakov *et al.*, 2014; Gajić *et al.*, 2012) versus field experiments showing shorter times of decades to centuries (Malghani *et al.*, 2014; Jones *et al.*, 2012). In addition, most of the field-studies conducted to investigated decomposition or mineralization used small plots which are often defined by rings or frames where soil tillage is not possible. In any case, we developed a new field incubation method (mini plot approach) to examine the mineralization of both char types in arable soils where tillage was allowed, with addition of zinc (Zn) as an inert tracer to be able to correct for blending or attenuation with the surrounding soil into the arranged mini-plots, e.g., due to tillage.

Hence, the aim of this study was to assess the stability of two char types under field conditions. For this, we conducted a 19-month *in-situ* field incubation with pyro- and hydrochar from *Miscanthus* at three agricultural field sites with different soil types in Northern Germany.

8.2 Materials and Methods

8.2.1 Production of pyrochars and hydrochars

The feedstock for both, hydrochar and pyrochar was above-ground biomass of the C_4-plant *Miscanthus x giganteus*. Pyrochar was carbonized in a Pyreg reactor at 750° for C 0.75 h. Hydrochar was produced with water (1:10, w/w) in a tabular reactor (3 m^3) at 200°C and 2 MPa for 11 h by AddLogicLabs / SmartCarbon (Jettingen, Germany). To catalyze the dehydration process in order to increase the C content in the solid product, citric acid powder was added to the *Miscanthus* (0.03 kg citric acid / 1 kg *Miscanthus*) (Wang *et al.*, 2010). Both chars were dried at 40°C and sieved <2 mm. The C and N content was determined via dry combustion (TruSpec, LECO Corp., St. Joseph (MI), USA). The oxygen and hydrogen contents of chars and the feedstock were determined with an elemental analyzer (Vario EL3, Elementar, Hanau, Germany). Element contents of chars (e.g. P, Ca, Mg, Na, K, S) of the prepared samples were analyzed using inductively coupled plasma-optical emission spectroscopy ICP-OES (Varian Liberty 150, Agilent, Palo Alto, USA). The pH-value of the chars was determined in 0.01 M $CaCl_2$ with a ratio of 1:5 (volume char/volume solution). Basic characteristics of feedstock, pyrochar, and hydrochar are listed in Table 8.1.

Table 8.1 General properties of feedstock material and the produced chars (n.d. = not determined).

Feedstock	Char type	Carbonization temperature [°C]	$\delta^{13}C$ value [‰ V-PDB]	pH ($CaCl_2$)	Ash content [%]	C [%]	O:C	H:C
Miscanthus	raw	-	n.d.	n.d.	2.9	46.3	0.64	1.61
	Hydrochar	200	-13.14	3.8	3.9	63.8	0.31	1.01
	Pyrochar	750	-14.22	9.0	15.0	81.8	0.07	0.15

8.2.2 Experimental design for in-situ field ageing

Three cropland sites in the North German lowland (mean annual temperature 8.8°C, around 600 mm precipitation) were chosen to incubate the chars *in-situ*. The three sites differ mainly in their soil texture (Table 8.2) and are located in Bortfeld (siltic Cambisol), Volkmarsdorf (cambic Planosol) and Querenhorst (arenic Planosol). All sites were managed according to common regional agricultural practice such as conventional tillage to a depth of around 25-27 cm and inorganic fertilization. The long-term C_3-crop rotations were i) barley (2012), winter wheat (cover crop), sugar beet (2013) (Querenhorst); ii) barley (2012), mustard (cover crop), sugar beet (2013) (Volkmarsdorf); iii) potatoes (2012), sugar beet (2013) (Bortfeld).

At all three sites, the two different types of chars were mixed into the soil in March 2013 in a randomized split-plot design. Mini-plots (plot size: 70 × 70 cm; plot depth: 25 cm) were triplicated

and divided into three blocks for each site so that every site consists of nine mini-plots: three were soil

Table 8.2 General properties of the soils used for the lab and field.

Site	Coordinates	Soil type	Sand [%]	Silt [%]	Clay [%]	C_{org} [%]	N_{tot} [%]	C/N	$\delta^{13}C$ value [‰ V-PDB] (±SE), n=9	pH ($CaCl_2$)
Bortfeld	52°28'N, 10°41'E	loamic Cambisol	57.0	37.1	5.9	0.93	0.13	7.3	-27.19 ± 0.19	6.4
Querenhorst	52°33'N, 10°96'E	arenic Planosol	74.7	18.0	7.3	1.13	0.13	8.8	-27.09 ± 0.05	6.8
Volkmarsdorf	52°36'N, 10°89'E	cambic Planosol	67.1	21.7	11.2	1.16	0.12	9.9	-27.40 ± 0.14	6.5

plots amended with pyrochar (soil+pyrochar+zinc), three with hydrochar (soil+hydrochar+zinc) and three plots served as control (soil+zinc). The distance between each mini-plot in one block was 200 cm. At each plot, soil was dug out and mixed with chars in a cement mixer in order to thoroughly mix the char and the soil. The char amendment was adjusted to double the soils' C-content, which corresponds to 100 Mg char ha^{-1}. Additionally, elementary zinc powder (particle size < 45 µm; Merck, Darmstadt, Germany) was added to the soil or soil-char mixtures at a concentration of 450 mg kg^{-1} soil as an inert tracer in order to increase the natural zinc-concentration seven-fold in the used soils to be able to correct for blending or attenuation with the surrounding soil, e.g., due to tillage. This led to a final concentration of around 500 mg Zn kg^{-1} soil, when assuming a background concentration of about 50 mg Zn kg^{-1} soil. The mini-plots were not physically separated from the field site but mixing with the surrounding soil was possible. We marked every plot centrically by putting one metal bar (5×1 cm) below the plough-horizon at a depth of 35-40 cm to make a precise relocation easier. In addition, every plot-center was georeferenced by GPS. The advantage of the mini-plots was that the farmers could manage the field sites with the research plots in the same way as every other field. Soil samples were taken in March 2013 right after mixing the soil with chars (designated as T_0). After seven months (October 2013), and after 19 months (October 2014), the second and third sampling was carried out (designated as T_1 and T_2) by taking five randomly distributed soil cores to a depth of 25 cm with a split-tube sampler (5 cm diameter) from each plot. Afterwards, samples were dried at 40°C and sieved to ≤ 2 mm and a subsample was finely ground for further analysis. Zinc concentrations (T_0, T_1, T_2) were extracted using microwave *aqua regia* digestion and determined using ICP-OES (Varian 725-ES, Agilent, Palo Alto, USA).

8.2.3 Correction of C-Stocks with the mini-plot approach

To correct C stocks from the remaining chars, a correction factor F_z was determined in order to correct for the mixing of surrounding soil into the mini-plots. This was done as follows:

$$F_z = \frac{C_{soil+char} - \left(1 - \frac{Zn_{0+1}}{Zn_0} \times 100\right) \times C_{ctrlsoil}}{C_{soil+char}}, \quad \text{(Eq. 1)}$$

where $C_{soil+char}$ and $C_{ctrlsoil}$ is the percentage C concentration of soil-char mixtures or control plots at the same block, respectively; Zn_0 and Zn_{0+1} is the percentage zinc amount at T_0 as well as at T_1 and/or T_2.

The C-stocks [Mg C ha^{-1}] for the topsoil (0-25 cm depth) were calculated as follows:

$$C_{stock} = F_z \times \left(C_{soil+char;\, ctrlsoil} \times Bd \times h\right), \quad \text{(Eq. 2)}$$

where Bd is the bulk density [g cm^{-3}] of the topsoil corrected for the stone content in the mini-plot and h the height [cm] of the taken soil sample.

The distribution of zinc within each single mini-plot was examined visually by comparing the remaining percentage zinc-concentration of the soil sample from the center with the samples from the edges (distance = 35 cm) (Figures A and B, see Supplement). A heterogeneous distribution of soil is indicated when the percentage concentration of zinc remaining in the soil at the center differs from the surrounding samples.

A ratio between percentage zinc and SOC remaining in soil after dilution at T_0, T_1, T_2 was used to test whether SOC contents of soils are more affected by dilution or by char mineralization of char (Figure S3, see Supplement).

$$R_{ZnC} = \frac{\%SOC_{char}}{\%Zinc}, \quad \text{(Eq. 3)}$$

where $\%SOC_{char}$ is the percentage concentration of total SOC subtracted from SOC of the control-plot at T_1 or T_2 relating to total SOC at T_0. %Zinc is the percentage concentration of zinc in soil at T_1 or T_2 relating to T_0. For example, the amount of chars in soil decreased despite decreasing zinc-concentration in soil when the ratio $R_{ZnC} < 1$. If $R_{Zn} > 1$ this is not reliable because it indicates an increase of char in soil or an inhomogeneous mixing of char, zinc and soil. When the amount of char decreased at the same rate as the zinc-concentration, then the $R_{ZnC} = 1$, which indicates no char

mineralization. The Gaussian error propagation was considered for zinc and C determination and is presented as a 95% confidence band around R_{ZnC} =1±0.5.

In a pre-study, we tested the effect of zinc on mineralization and microbial biomass. Soil samples of two of the three experimental sites were incubated in triplicate after being mixed with five different concentrations of zinc (control = background zinc concentration of the soil, Zn_{c1} = 200 mg Zn kg^{-1} soil, Zn_{c2} = 500 mg Zn kg^{-1} soil, Zn_{c3} = 1000 mg Zn kg^{-1} soil and Zn_{c4} = 6000 mg Zn kg^{-1} soil). The soil respiration and microbial biomass (using SIR) were measured according to Heinemeyer *et al.* (1989) for the different zinc-concentrations. We found no significant effect of zinc on the mineralization rates up to a zinc concentration of Zn_{c3}. However, we found a slight decreasing trend in the microbial biomass-C in the order Zn_{c1}>Zn_{c2}>Zn_{c3} but these differences were not significant (Fig. C). Only microbial biomass-C in the highest zinc-concentration treatment (Zn_{c4}, which is twelve-fold higher than the zinc-concentration used in our field trial) was significantly different from the lower zinc treatments.

8.2.4 Determining the $\delta^{13}C$ signature of sampled chars and calculating the proportion of char-derived C

To distinguish between char-derived C and native SOC, the $\delta^{13}C$ signatures of the pure chars, the control soils, and soil-char mixtures were determined using stable isotope ratio mass spectrometry (IRMS) (Delta plus, Thermo Fisher Scientific, Bremen, Germany) coupled to an elemental analyzer (CE Instruments FLASH EA 1112, Thermo Fisher Scientific, Bremen, Germany). The $\delta^{13}C$ signatures were determined for one of five soil samples from a mini-plot. We used a mixing model (Bernoux *et al.* (1998), Gregorich *et al.* (1995)) to estimate the mass balances for both char-C and native SOC for every sampling date:

$$X = \frac{\delta C_{soil+char} - \delta C_{soil}}{\delta C_{char} - \delta C_{soil}} \times 100, \qquad \text{(Eq. 4)}$$

where X is the proportion of C derived from char, $\delta C_{soil+char}$ is the $\delta^{13}C$ value for soil mixed with char, δC_{soil} is the $\delta^{13}C$ value from the non-treated control soil and δC_{char} is the $\delta^{13}C$ value of the respective char type.

8.2.5 Mean decomposition time calculations of chars in soil

For each of the five samples per mini-plot the corrected leftover char in soil at T_0, T_1, and T_2 per plot was fitted to a one-pool-decay model to determine the time after which 50% (half-life period) and 1% of incubated char is leftover as well as the mean residence time (MRT):

$$Char_{leftover} = a \times e^{-k \times t}, \qquad \text{(Eq. 5)}$$

where a = is the initial amount of char at T_0 (100%) and k is the decay constant.

8.2.6 Statistical analyses

Statistical analyses were conducted using R 3.2.2 (RCoreTeam, 2015). As the C-stock data were unbalanced repeated measures from a randomized split-plot design, a linear mixed effects model from R package *lme4* (Bates *et al.*, 2015) was fit to the data. We used C stocks as dependent variable and char type, site, time, char type×site and char type×time as fixed factors. Random effect was the block in which the plots were established, so the intercept is free to vary across the blocks. The results of the analysis of variance (ANOVA) are shown in Table 8.3. The model with the best fit was chosen with the 'dredge'-function of the *MuMIn*-package (Bartoń, 2015). The best model was chosen by comparing the Akaike's information criterion (AIC) of all possible models. Significance of differences between treatments' changes in Zn-concentrations as well as C-stocks were analyzed using ANOVA followed by Tukey's Post-Hoc test ($p<0.05$).

Table 8.3 Multifactorial ANOVA about significant influences of tested treatment factors on C-stocks.

Factor	DF	*F*-value	*p*-value
Time	1	10.516	<0.01
Site	2	0.024	0.97
Char type	2	139.4	<0.01
Site × char type	4	7.311	<0.01
Time × char type	2	5.389	<0.01

8.3 Results

8.3.1 A new type of field incubation with an inert tracer

For the first time a mini-plot field incubation approach was used that allowed the stability of organic amendments under common agricultural practice conditions to be investigate. This approach minimized the management effort for field incubation since it can be conducted on practicing cropland without presenting any obligations to the management of the farmer. Since the soil of the plots was not physically separated from the surrounding soil using any type of wall, the surrounding soil was mixed into the plots during tillage operations. A fixed amount of zinc was added to the soil together with the char for all treatments to be able to determine this dilution with surrounding soil. A correction factor based on the zinc concentration as inert tracer was used to correct for the C-content of SOM and char. Figure 8.1 shows the percentage decrease in the zinc concentration over the experimental duration. The initial zinc concentration was significantly reduced from T_0 to T_1 (60% of the initial amount of zinc) and to T_2 (20%) at all sites. This was an unexpectedly high dilution that was also due to the fact that the plots were shallower than the tillage depth. The zinc concentration varied largely within the mini-plot with 16 to 72% zinc remaining in the soil at T_1 and <1% to 31% zinc remaining at T_2 (Figures A and B, see Supplement). Thus, the variability was larger at T_1 as compared to T_2. With tillage operations also soil material below the

mini-plots was mixed in and this vertical dilution was up to about up to 17%, accounting for roughly one fifth of the total zinc dilution in the mini-plots.

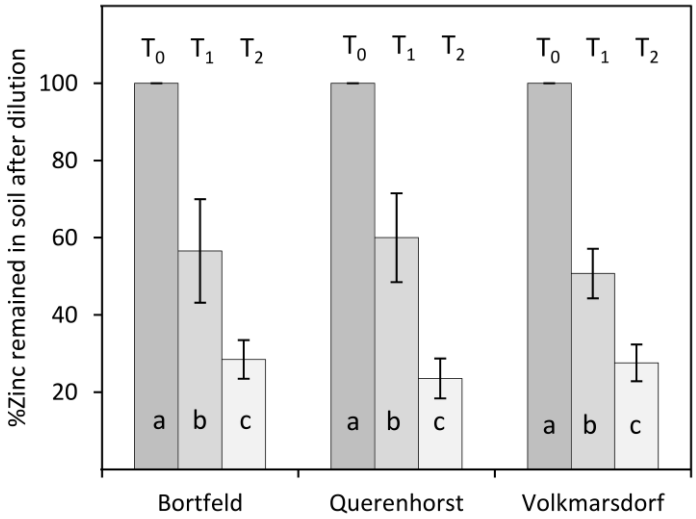

Figure 8.1 Change of the zinc concentration in the used soils after 7 month (T_1) and 19 month (T_2) due to dilution with the surrounding soil (e.g. through ploughing) (mean ± SE; n=9). Different letters indicate significant differences between sampling dates of the %amount of zinc. Different capital letters indicate significant differences between sampling dates of char derived C ($p<0.05$).

8.3.2 Char-C mineralization and modeled turnover time

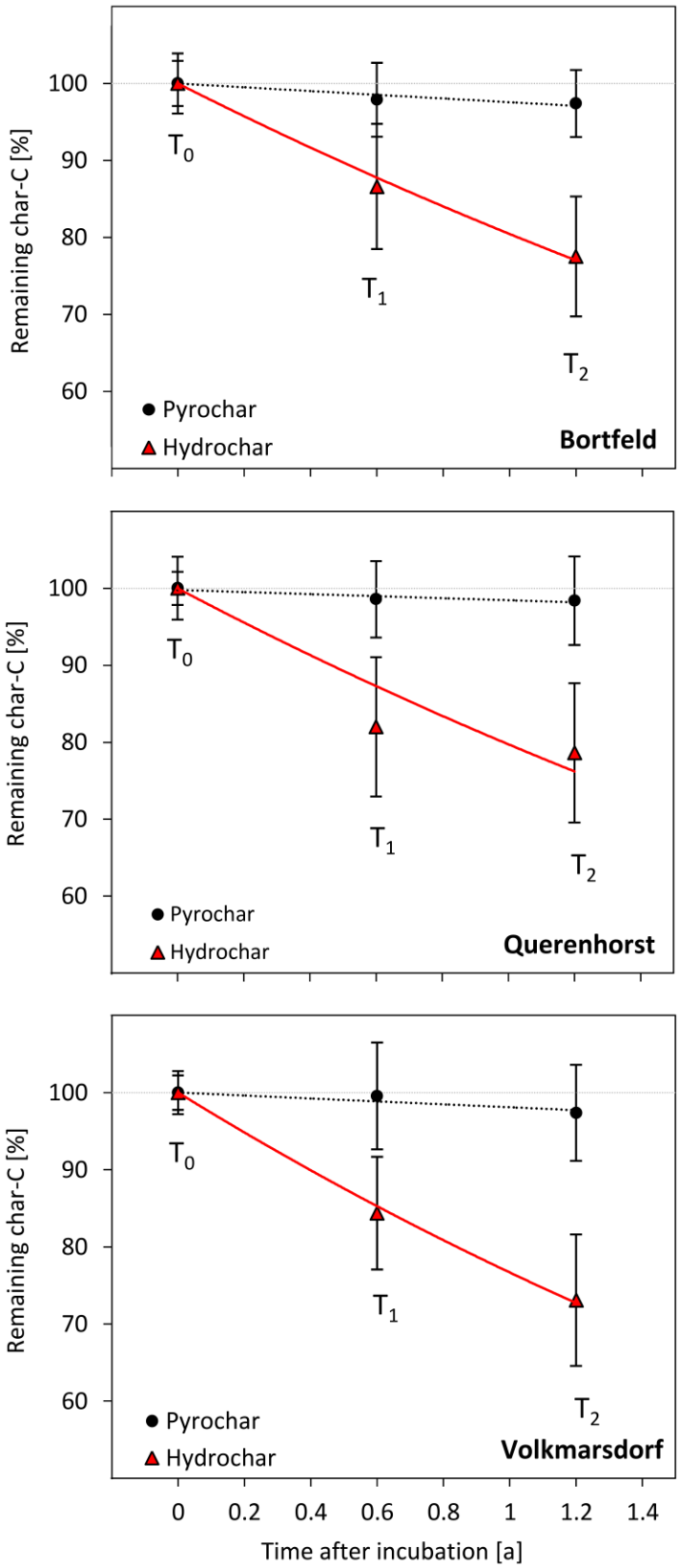

Figure 8.2 Remaining C as % of initial char-C added to soil for the three sampling times T_0, T_1 and T_2 and the modeled decomposition with the exponential decay function (n=3).

Figure 8.2 shows the remaining char-C after 7 and 19 months. While pyrochar-C did not significantly change over time, hydrochar-C was significantly reduced between T_0 and T_2 (Figures 8.2 and 8.3). We found that about 70 to 80% hydrochar-C was left over after 19 months. Pyrochars showed no significant mineralization. Isotopic mass balance of the bulk soil indicated that the native SOC content of all three sites did not change significantly and ranged between 34 and 40 Mg C ha^{-1} in 0 to 25 cm depth (Figure 8.3). At all three field sites, the hydrochar-C decreased by 22 to 27% of the initially added hydrochar-C from T_0 to T_1 (month 0 to 7) and again by 17 to 23% of the remaining hydrochar-C at T_1 from T_1 to T_2 (months 8 to 19). In total, during the 19-months field-trial, 38 to 42% (15-19 Mg C ha^{-1}) of hydrochar-C was mineralized with similar rates. From the originally added hydrochar-C at all three experimental sites, 58-62% of the originally added hydrochar-C remained in the soils after 19 months.

For pyrochar, the ratio between percentage SOC and zinc remaining in soil is 1±0.1 which indicates no mineralization of pyrochar during the experimental period at all sites (Figures D) but also slight mineralization for some samples where R_{ZnC} was <1. Furthermore, for hydrochar, the R_{ZnC} was <1 for all zinc dilution stages indicating a decomposition of hydrochar.

A one-pool decay model was used to estimate char Cs' half-life and MRT. On average over all sites, pyrochars' MRT was determined as 60 ± 6 years (Table 8.4). The mean residence time for hydrochar was 4 ± 0.2 year. After 274 ± 30 and 20 ± 1 years, only 1% of applied pyrochar and hydrochar would remain respectively. But a large variability among the replicates was observed at all sites. The MRT for hydrochar ranged between 4 and 5 years, pyrochars ranged between 33 and 91 years over all sites. But within one site, the variability was also large: While, e.g., at the Volkmarsdorf site, the shortest MRT for pyrochars was 34 years for block No. 2, the MRT for block No. 1s' was about 91 years.

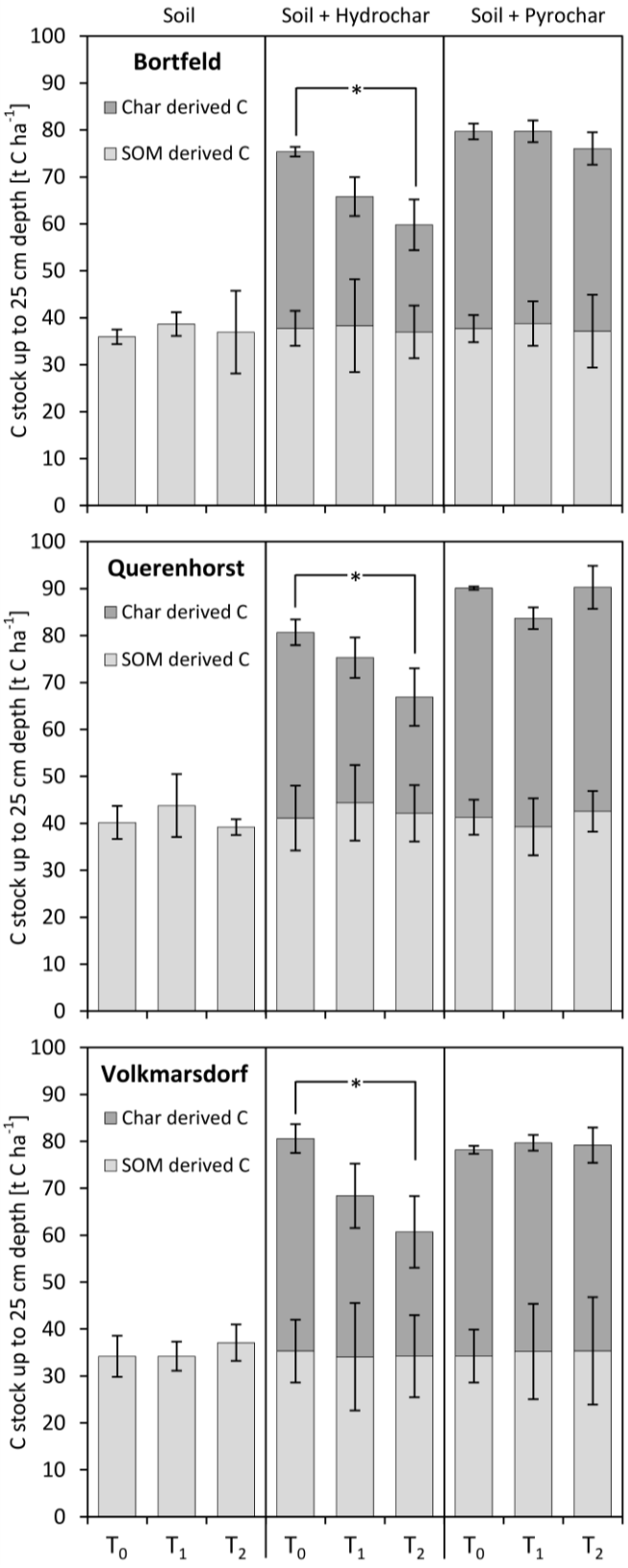

Figure 8.3 Carbon stocks for the three experimental sites and sampling dates (T_0, T_1, T_2) using isotopic mass balance of the bulk soil. Differences between sampling dates of char and/or SOM derived C was tested with Tukey's post-hoc test. Significant differences are indicated by * ($p<0.05$, mean ± SE, n=3).

Table 8.4 Residence times of chars for every experimental site. Calculated values of the exponential decay function (Eq. 5) are indicated as means and standard error (SE) of five samples per mini-plot within each block. Model fit was characterized with the root mean square error (RMSE) and the adjusted correlation coefficient (Adj R^2). λ½ is the half life time of the chars and MRT is the mean residence time.

Site	Char type	Block	a (SE) [%]		k (SE)		**RMSE [%]**	**Adj R²**	50% char leftover (λ½) [a] (SE)	MRT [a]	1% char leftover [a] (SE)
Bortfeld	Hydrochar	1	98.77	(5.1)	0.24	(0.07)	**3.19**	**0.64**	2.9	4.2	19.1
		2	100.17	(0.3)	0.22	(0.01)	**0.34**	**0.95**	3.2	4.6	21.3
		3	99.12	(2.9)	0.21	(0.05)	**1.77**	**0.98**	3.3	4.7	21.8
							Average for all blocks:		**3.1 (0.1)**	**4.5 (0.1)**	**20.7 (0.7)**
	Pyrochar	1	99.32	(4.7)	0.02	(0.02)	**3.02**	**0.82**	46.2	66.7	306.3
		2	98.63	(3.3)	0.01	(0.05)	**3.19**	**0.55**	53.3	76.9	353.5
		3	96.97	(6.8)	0.01	(0.09)	**6.97**	**0.76**	49.5	71.4	328.2
							Average for all blocks:		**49.7 (1.7)**	**71.7 (2.4)**	**329.3 (11.1)**
Querenhorst	Hydrochar	1	93.56	(17.4)	0.24	(0.29)	**10.72**	**0.17**	2.9	4.2	19.1
		2	96.83	(7.7)	0.22	(0.11)	**4.81**	**0.55**	3.2	4.6	21.2
		3	107.75	(22.5)	0.19	(0.34)	**13.81**	**0.88**	3.7	5.4	24.8
							Average for all blocks:		**3.3 (0.2)**	**4.7 (0.3)**	**21.7 (1.4)**
	Pyrochar	1	96.44	(8.2)	0.03	(0.12)	**13.13**	**0.11**	25.7	37.0	170.2
		2	101.48	(3.4)	0.02	(0.05)	**6.93**	**0.62**	46.2	66.7	306.3
		3	100.11	(2.2)	0.03	(0.07)	**5.33**	**0.40**	23.1	33.3	153.2
							Average for all blocks:		**31.7 (6.0)**	**45.7 (8.6)**	**209.9 (39.6)**
Volkmarsdorf	Hydrochar	1	102.89	(9.7)	0.25	(0.09)	**9.81**	**0.73**	2.8	4.0	18.3
		2	99.72	(8.9)	0.26	(0.26)	**32.68**	**0.92**	2.7	3.9	17.9
		3	103.84	(10.4)	0.28	(0.15)	**10.08**	**0.54**	2.5	3.6	16.7
							Average for all blocks:		**2.7 (0.1)**	**3.8 (0.1)**	**17.7 (0.4)**
	Pyrochar	1	97.97	(4.7)	0.01	(0.07)	**10.99**	**0.00**	63.0	90.9	417.7
		2	100.74	(1.7)	0.03	(0.02)	**5.11**	**0.44**	23.9	34.5	158.5
		3	100.04	(0.1)	0.02	(0.00)	**2.43**	**0.20**	40.8	58.8	270.3
							Average for all blocks:		**42.6 (9.2)**	**61.4 (13.3)**	**282.2 (61.3)**
All sites					Hydrochar				**3.0 (0.1)**	**4.4 (0.2)**	**20.0 (0.8)**
					Pyrochar				**41.3 (4.5)**	**59.6 (6.4)**	**273.8 (29.6)**

8.4 Discussion

8.4.1 Potential of chars to sequester C in soils

Hydrochar stability

During 19 months *in-situ* field incubation, 38 to 42% of the originally added hydrochar-C was lost, which confirms a relatively high mineralization potential of hydrochars (Malghani *et al.,* 2014; Gajić *et al.,* 2012). Our results were corroborated by other studies which found 68-88% hydrochar-C loss after a one year laboratory incubation and 48-77% after one year field incubation study (Malghani *et al.,* 2014; Gajić *et al.,* 2012). Large amounts of oxygen-containing functional groups make hydrochar sensitive towards mineralization when applied to soils (Eibisch *et al.,* 2013; Sevilla *et al.,* 2011). However, mineralization rates for non-carbonized cellulose could be up to 95% decomposition of the original plant residues within 8 weeks (half-life period of 2 weeks)(Hadas *et al.,* 2004). Litterbag studies estimated that 40-54% of *Miscanthus* leaves were decomposed within one year (Amougou *et al.,* 2012; Yamane and Sato, 1973). This indicates that with carbonization of *Miscanthus,* the decomposition time could at least be doubled. Studies about hydrochar stability using the two-pool decomposition model show that mineralization generally occurred in two steps: i) the main pathway for hydrochar-C loss is via CO_2 through easily degradable C sources during the first two months after application to soil. Malghani *et al.* (2014) reported hydrochar-C losses of about 37% when added to soil as CO_2 after a one year field lysimeter experiment. ii) A second pathway for less degradable C sources is indicated by DOC in leachates (Hoekman *et al.,* 2011; Malghani *et al.,* 2013). The decomposition time for this pool is between years and decades. We used a one-pool decay model which cannot distinguish between the decomposition of the labile and stabile C pools. However, in our study the decomposition rates did not change over the 19-month incubation period. This indicates that the mineralized C source is rather homogeneous. No two pool-models are required to model the mineralization dynamics.

One critical aspect of labile C (hydrochar) addition to soils is the feedback on the decomposition of native soil-C as priming (Keith *et al.,* 2011; Kuzyakov, 2010). Malghani *et al.* (2014) observed both, positive priming in the first 3 months after hydrochar application, and negative priming after the first 3 months. *Miscanthus*-derived C in SOM has an MRT of between 1.0 and 3.5 years when it was added to soil without charring (Foereid *et al.,* 2004). Our estimated MRT for *Miscanthus* converted to hydrochar ranged between 1 and 9 years and the half-life between 1.2 to 5.8 years. The estimated MRT is in the range reported in other studies (5.5 and 8.3 years) (Naisse *et al.,* 2015; Gajić *et al.,* 2012), but shorter than reported by Malghani *et al.* (2014). They estimated a half-life period of around 19 years for hydrochars gained from corn silage by two carbonization steps with an initial temperature of 230°C and a second at 180°C applied to a coarse and a fine soil in a one

year field experiment. Compared to this, our hydrochar was produced at 200°C by single carbonization of *Miscanthus*, which may result in a less stable char matrix as indicated by a H/C ratio of 1.01 as compared to a ratio of 1.33 for the hydrochar used by Malghani *et al.* (2014). Nevertheless, due to its medium fast mineralization, hydrochar continuously releases NO_3^-, NH_4^+, and PO_4^{3-} (Gronwald *et al.*, 2015) which implies the potential to use hydrochar as a slow-release fertilizer.

Pyrochar stability

Pyrochar showed no significant decomposition over all sites during the 19-months incubation time. This implies the assumption that pyrochar is a highly recalcitrant C storage medium. There are recent studies on char-C stability which support our findings about pyrochar (Bamminger *et al.*, 2014; Kuzyakov *et al.*, 2014; Malghani *et al.*, 2013; Nguyen *et al.*, 2010; Zimmerman, 2010; Kuzyakov *et al.*, 2009). Fang *et al.* (2014) reported a pyrochar-C mineralization of 0.3-2.7% within a 12-month laboratory incubation study with pyrochars from wood biomass of *Eucalyptus salinga* produced at 450-550°C mixed with soil (2%, w/w). Kuzyakov *et al.* (2014) found that only around 3% of char-C was mineralized within the first 12 months of an 8.5-year laboratory incubation study with char from *Lolium perenne* carbonized at 400°C under oxic conditions. A mineralization rate of 62-65% was reported in an 28-moths laboratory incubation study by Hilscher and Knicker (2011), who carbonized *Lolium perenne* at 350°C under oxic conditions. The higher char-C mineralization in the two last studies as compared to this study can be related to the i) grass-derived char, which degrades more easily than chars e.g. from wood (Zimmerman, 2010), ii) the production conditions were different from ours, e.g., we used a higher carbonization temperature (750°C) without oxygen (pyrolysis) , and iii) *Miscanthus* is more lignified than *Lolium perenne*. In addition to feedstock type, the char production temperature affects the differences in char-C degradability due to different degrees of aromatic C condensation which increased with increasing carbonization temperatures (Singh *et al.*, 2012; McBeath and Smernik, 2009). Furthermore, one critical and important aspect is the experimental duration: when mineralization studies with chars are too short, the amount of labile pools would be mainly affect the calculations of decomposition times and thus, the labile pool may be overestimated (Lehmann and Joseph, 2009). Pyrochar addition may also affect native soil-C and its decomposition via positive as well as negative priming. However, pyrochar addition to soil suppressed mineralization of native SOC by up to 69% due to negative priming (Lu *et al.*, 2014). It has been shown that pyrochar contains very little microbial available C, which implies a negligible importance of pyrochar as a C source for microorganisms (Kuzyakov *et al.*, 2014; Kuzyakov *et al.*, 2009). Other studies showed that pyrochar addition could increase soil-C mineralization and microbial biomass due to the presence of additional nutrients released to soil (Zhao *et al.*, 2015; Kolb *et al.*, 2009). Even though mineralization rates were found to be low, pyrochar-C can be

mineralized to CO_2 or leached as DOC through abiotic and biotically induced processes (Fang *et al.*, 2014; Liu *et al.*, 2013; Lehmann and Joseph, 2009; Cheng *et al.*, 2006). Also pyrochars comprise a labile C pool, consisting mainly of glycol and phospholipids which can be rapidly decomposed (Kuzyakov *et al.*, 2014). Around 0.3 – 1.0% of pyrochar can be lost via leaching as extractable soluble and colloidal fractions downwards the soil profile by 5 to 25 cm within two years e.g. with bioturbation or water percolation (Abiven *et al.*, 2011; Major *et al.*, 2010). In our study we did not sample the horizon below the ploughing horizon to which the char was applied to verify these pyrochar downward movement processes.

Our estimated MRT for pyrochar ranged between 12 and 100 years and the half-life period between 8 and 54 years with a large variance for each replicate per site. Nevertheless, the calculations based only on some replicates where we observed pyrochar mineralization. The large uncertainties of the MRT estimates indicate that the experimental period was too short to obtain sufficient data to fit a trustworthy model. The MRT we found for pyrochar is in general shorter than reported from incubation studies that range between 40 and 4000 years (Fang *et al.*, 2014; Kuzyakov *et al.*, 2014; Hamer *et al.*, 2004). However, the discrepancy between MRTs estimated from incubation studies showing life-times of millennia versus field experiments showing shorter times of decades to centuries remains large (Kuzyakov *et al.*, 2014). Furthermore, most of the estimated MRTs based on laboratory incubation studies using ^{14}C-approaches which are not *per se* comparable to studies using ^{13}C.

8.4.2 The new mini-plot methods for field incubations – advantages and disadvantages

This was the first study applying a new mini-plot approach on non-experimental field sites. The incubation approach could be applied even if the substrate of interest was not available in quantities that are required for conventional field incubation studies. Moreover, the plots were not physically separated from the rest of the field, e.g., by trenches or walls. Farming practices could be continued without any adjustments due to the mini-plots. Thus, this method can be easily applied to study the fate on any type of soil amendment. In order to account for the dilution of mini-plot soil and substrate with surrounding soil mainly during tillage operations, an inert tracer (zinc) was used to be able to correct for this dilution. Decreasing zinc concentrations indicated a significant dilution with surrounding soil by up to 80% of initial soil after 19 months. The variability of the zinc content within each plot was higher at T_1 compared to T_2 indicating that the mixing of soil, zinc and char worked out well and there was no evidence of fractionation of zinc and char with erosion or leaching. We estimate that around one fifth of non-sampled soil below the sample-depth could dilute each soil sample and thus increase the error at each sample date and plot. Slightly larger plot size and plots as deep as the maximum ploughing depth would help to reduce the dilution within the mini-plots. The dilution vs. real decomposition-ratio R_{ZnC} showed that pyrochars were mineralized

with rates not significantly different from zero ($R_{ZnC} \approx 1$). The R_{ZnC} of 0.35 to 0.97 for hydrochars indicates that mineralization rates were significant and detectable with this method. The dilution of mini-plot soils and zinc may occur through tillage or bioturbation into soil layers below the application horizon, which was not sampled. A precise estimation of the zinc concentration is essential since the zinc-based correction factor affected i) the calculations of char-C mineralization and thus the distinction between the dynamics of SOM-C and char-C as well as ii) the estimated turnover time of the two char types. In any case, the advantage of this new method lies in the low material cost, as the production of chars is still quite expensive and for the mini-plot method only small quantities of char are required. The plots require no particular continuous maintenance work but can be managed by the farmers in the course of their normal activities. One disadvantage of the method is the necessity to analyze the zinc-content for all samples, which would not be necessary in a conventional field trial in which a soil dilution as described does not take place. We tested the effect of different zinc concentrations on mineralization rates and only detected zinc effects at concentrations which were twelve-fold higher than the applied zinc concentrations of our study. Any additional microbial effects cannot be ruled out and require further attention. Thus, the application of the new mini-plot method with zinc as an inert tracer seems to be a feasible, reliable and economically sound option to investigate the stability of chars or other substrate under field conditions given sufficiently long-incubation times.

8.5 Conclusions

Pyrochar applied to soils can be an option to sequester atmospheric C on the long-term, in contrast to hydrochar. The main questions regarding this option are the availability of biomass for char production and the economic and greenhouse gas costs for its production and application. Without additional synergetic benefits of char applications to agricultural soils, char application will not be adopted by farmers. The low stability of hydrochar with a higher proportion of functional groups and reactivity may offer such an additional benefit. Plant available nutrients may be slowly released from hydrochar during its mineralization, wherefore hydrochar can be also used as slow-release fertilizer.

Any study on the stability of organic substrates in soils is biased if it is conducted in the laboratory instead of in the field. The mini-plot method applied in this study offers a new opportunity to study mineralization dynamics in the field *in-situ* with very low operational costs. We recommend deep enough (≥max. tillage depth) and slightly larger plot-sizes to reduce the dilution with surrounding soil material within each plot.

8.6 References

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CHAPTER 9 SYNOPSIS AND CONCLUSIONS

9.1 Overview: Main results of the studies

Table 9.1 Overview on each study and its' objectives as well as their main conclusions.

Study	Objectives	Main Conclusion
Batch-equilibrium experiments (**Chapter 6**: Effects of fresh and aged chars from pyrolysis and hydrothermal carbonization on nutrient sorption in agricultural soils).	**1.** Estimating the sorption potential of chars on nutrients	**1.** In the laboratory batch-experiment, only pyrochars showed the ability to effectively retain nitrate, ammonium, and phosphate.
	2. Investigating the sorption potential of fresh *vs.* aged chars on nutrients	**2.** The nutrient retention effect seems to be of very limited duration. After 7 months in the field, around 60 to 80% of the adsorption capacity of pyrochar was lost.
		→ The results cast doubt on the efficiency of char application to minimize the problems of nutrient leaching from agricultural soils to the groundwater and adjacent ecosystems.
NH_3 volatilization experiment (**Chapter 7**: Mitigation of ammonia emissions from manures: Acidification is more effective than char application)	Estimate the reduction potential of pyrochar and hydrochar on NH_3 emissions from organic manures	**1.** The effect of pyrochar and hydrochar on NH_3 emissions from organic manure was mainly driven by char-induced pH changes.
	Assessing which char-mechanism has more influence on NH_3 volatilization from manures: pH or adsorption.	**2.** The pH management of manure by char addition to reduce NH_3 emissions is rather ineffective as compared to direct acidification. To reach the same NH_3 reduction potential as acidification, a large, and therefore expensive, amount of char would be required.
		→ No recommendation for the use of char to reduce NH_3 volatilization from organic manure.
Char stability experiment (**Chapter 8**: Stability of pyrochar and hydrochar in different agricultural soils - a new field incubation method)	Assessing the hydrochar and pyrochar stability against mineralization.	**1.** Pyrochar applied to soils can be an option to sequester atmospheric C on long-term, contrary to hydrochar.
		2. Plant available nutrients may be slowly released from hydrochar during its mineralization, wherefore hydrochar can be also used as slow-release fertilizer.
		→ Without additional synergetic benefits of char applications to agricultural soils, char application will not be adopted by farmers. The low stability of hydrochar with a higher proportion of functional groups and reactivity may offer such additional benefit.

The present study aimed at investigating the consequences for char application to the environment, especially to the 'critical zone' soils. Most current studies on char application to soil do not systematically compare different types of char from the same feedstock. Furthermore, most studies were conducted in laboratory-setups which implies a systematic bias when results were transfer into the 'real world'. Anyhow, before specific types of chars were added to soils, one mayor question has

to be asked: For which benefit do we want to use chars? The main discrepancy regarding the benefit was brought to the point 'stability *versus* functionality' by Schimmelpfennig and Glaser (2012) with the contrasts:. If the expected benefit of chars is to sequester atmospheric C in soils, then a char type has to be used which is stable against mineralization or degradation. But this type of char may be less useful to get further nutrients from its matrix because this char wouldn't degrade. Otherwise, nutrient-rich chars are useful to release nutrients from the char matrix into the rhizosphere but, however, this char types are labile and highly vulnerable against degradation. Therefore, it was investigated if soil amendment with either pyrochar or hydrochar is useful for C-sequestration and/or mid-term nutrient management (Chapter 6&8). Moreover, N-management in agriculture gets raising importance. For this, the influence of char application to organic manures was tested to assess if chars has a reducing effect on NH_3 volatilization and which char-mechanisms are more responsible: pH or adsorption (Chapter 6&7).

9.2 Stability vs. functionality: Hydrochar and pyrochar for nutrient management and/or C-sequestration in agricultural soils *(Combining the results of the laboratory batch-experiments and the field study from Chapter 6 with the results of the field study from Chapter 8)*

The laboratory batch experiments of Chapter 6 presented the results on the potential sorption capacity for NO_3^-, NH_4^+, and PO_4^{3-} of nine different chars (pyrochars from digestates, *Miscanthus*, woodchips; hydrochars produced at 200 and 250°C from digestates, *Miscanthus*, woodchips) mixed with two soils (silty loam and sandy loam). Furthermore, in a field study, a systematically comparison of pyrochar and hydrochar from the same feedstock (*Miscanthus*) were *in-situ* incubated at three agricultural sites in Northern Germany to assess their stability against mineralization over a 19-month period. The objectives of both studies were to i) estimate the sorption potential of chars on nutrients and to ii) investigate the sorption potential of 'fresh' *vs*. 'aged' chars on nutrients as well as to iii) erstimate the stability of pyrochar and hydrochar during a 19-month *in-situ* field incubation.

At the application date of chars to soil (T_0) and after seven months (T_1), soil samples were taken to estimate the sorption potential on nutrients for 'fresh' and 'aged' chars in an another batch experiment. In addition, from the same field study soil samples from T_0, T_1 and additionally 19 months after application (T_2) were used to determine SOC-content and $\delta^{13}C$ of bulk soil to calculate the proportion of char-C remained in soil to assessing the char stability (Chapter 8). A one-pool decay model was fit to the data to estimate the mean residence time for pyrochar and hydrochar.

Generally, nutrient retention potential of char is a result of cation or anion exchange combined with the large surface area, internal porosity and polar and nonpolar surface sites of functional groups (Hale *et al.,* 2013; Laird *et al.,* 2010; Lehmann and Joseph, 2009). In the laboratory batch experiment of Article 1, pyrochars showed the highest ability to retain NO_3^-, NH_4^+, and PO_4^{3-} which

confirms **hypothesis H_1**. Previous studies indicate that increasing carbonization temperature results in higher SSA of the produced char (Cantrell *et al.*, 2012), which in turn leads to higher adsorption (Hale *et al.*, 2013; Yao *et al.*, 2012; Lehmann and Joseph, 2009). Pyrochar showed an increasing adsorption potential for NO_3^- and NH_4^+ in the order (lowest to highest) digestates < *Miscanthus* < woodchips. The adsorption potential for PO_4^{3-} was in the order *Miscanthus* < woodchips. For digestates, PO_4^{3-} was leached out in high amounts. The digestate feedstock and digestate carbonized to pyrochar and hydrochar contained 10 times more phosphorus than the chars produced from the other two feedstock materials, which explains the high PO_4^{3-} leaching from the char matrix itself. This partly confirms **hypothesis H_2**. However, the results from Article 1 and results from previous studies showed anion adsorption, the processes of which are not yet fully understood. Chun *et al.* (2004) and Chen *et al.* (2008) disproved the ability of PO_4^{3-} ions to bind with negatively charged char surface functional groups like hydroxyls, carbonyls, carboxyls, and phenolics. However, Sarkhot *et al.* (2013) proposed that the exchange of surface hydroxyl groups on char with PO_4^{3-} induces a pH-controlled anion sorption capacity. Another mechanism is the ability of PO_4^{3-} ions to form bridge bonds using the residual charge of electrostatically attracted or ligand-bonded multivalent cations (Ca^{2+}, Mg^{2+}, Al^{3+},Fe^{3+}) (Mukherjee *et al.*, 2011).

The adsorption potential was higher in sandy loam compared to silty loam. However, the NH_4^+ adsorption of pyrochars was controlled by the soil type of the soil–char mixture. There was some NH_4^+ retention on sandy soils, but no pyrochar effect or even NH_4^+ leaching from the loamy soil. The PO_4^{3-} retention capacity of pyrochars strongly depended on the pyrochar feedstock with large PO_4^{3-}leaching from digestate-derived pyrochar and some adsorption capacity from woodchip-derived pyrochar. Therefore, while only the adsorption of NH_4^+ and NO_3^- are higher in sandy loam than in silty loam and the PO_4^{3-} retention capacity was more feedstock determined, the results partly confirmed **hypothesis H_3**. The adsorption capacity of chars for nutrients interacts with the amended soil type. Generally, soil's adsorption capacity for NO_3^- , NH_4^+ , and PO_4^{3-} is determined by pH, CEC, AEC, SSA, organic matter content, and soil texture. Hale *et al.* (2011) suggest a decreased reduction in the sorption capacity of chars caused by blocking of sorption sites by DOC, which could leach out from soil and may adsorb to chars. The solubility of DOC can be increased by increasing negative charge on the DOC due to a raised pH through char application to soils (Alling *et al.*, 2014). In Article 1, application of pyrochars led to a stronger rise in pH in the silty loam than in the sandy loam. According to Hale *et al.* (2011), this could have induced higher DOC solubility in the sandy loam and the leached DOC was adsorbed by pyrochars, resulting in blocked binding sites. Further, the soils tested in this study differed strongly in their texture and CEC. The silty loam contained higher amounts of multi-layer clay minerals, which led to higher adsorption competition between char and clay mineral surfaces.

In the field study of Chapter 6, a surprisingly rapid loss of the chars' adsorption capacity on all nutrients after field application of the chars was found. For all sites and for hydrochar and pyrochar, the adsorption capacity was reduced by 60–80% to less or no nitrate and ammonium adsorption. Amending the soils with char led to adsorption of NO_3^- for both pyrochar and hydrochar at all experimental sites. However, adsorption was higher for pyrochars than hydrochars. Pyrochar reduced NO_3^- leaching by up to 58% relative to the control, while hydrochar reduced leaching by up to 25%. Little relative NH_4^+ adsorption was found for fresh hydrochar and for aged hydrochar in the field. The relatively low adsorption capacity of hydrochars sometimes even changes to NH_4^+ leaching. Explanations for the decreasing nitrogen adsorption capacity of pyrochar may include the following: (a) binding sites of both types of char may be blocked with organic matter or mineral particles such as clay, and (b) binding sites of pyrochar may be reduced by microbial degradation changing the char's surface properties, which in turn leads to a diminished number of negatively charged binding sites (Cheng *et al.,* 2008; Glaser *et al.,* 2000). However, for this study, a decreasing adsorption capacity of chars could not explain with these mechanisms. The effect of pyrochar aging on PO_4^{3-} adoption was different from the other nutrients: aging increased the PO_4^{3-} retention capacity of pyrochar soil mixtures at all three sites from leaching or no effect (T_0) to adsorption (T_1). The effect of hydrochar on PO_4^{3-} was minor. Hydrochar was a source for PO_4^{3-} in most soils with no consistent changes due to char aging. These results led to reject **hypothesis H_4** because aged chars i) did not show any higher adsorption capacity and ii) adsorption was chaged into a release of nutrients such as NH_4^+ and PO_4^{3-} from chars to soil. The increased adsorption capacity of char for PO_4^{3-} may thus be partly a result of initially bound PO_4^{3-} that was leached from fresh chars (T_0) and was leached less after 7 months (T_1).

With regard to the investigation of char stability (Chapter 8) at the same experimental field sites used for Chapter 6, hydrochar showed a significant mineralization by up to 25% of the originally added hydrochar-C to soil during the 19-month *in-situ* field incubation. Furthermore, pyrochar-C did not change over time and there was no difference in decomposition dynamics of the chars among the three field sites with different soil types. This implicates the assumption that pyrochar is a highly recalcitrant C storage medium which confirms **hypothesis H_7**. Moreover, there was no decline in decomposition rates with time but the data were well fitted with a linear one-pool decay model. The model derived mean residence times were 5±1 years for hydrochar and (with larger uncertainty) 42±10 years for pyrochar.

For hydrochars, other studies reported the physical structure and chemical properties result in a lower recalcitrance towards microbial degradation compared to pyrochars (Bargmann *et al.,* 2014a; Hale *et al.,* 2011; Steinbeiss *et al.,* 2009). Large amounts of oxygen-containing functional groups make hydrochar sensitive towards mineralization when applied to soils (Eibisch *et al.,* 2013; Sevilla

et al., 2011). Studies about hydrochar stability using the two-pool decomposition model showing that mineralization generally occurred in two steps: i) the main pathway for hydrochar-C loss belongs to CO_2 through easily degradable C sources during the first two months after application to soil (labile pool). ii) A second pathway for less degradable C sources is indicated by DOC in leachates (stable pool) (Fang *et al.*, 2014; Liu *et al.*, 2013; Lehmann and Joseph, 2009; Cheng *et al.*, 2006). Regarding the char-use as C-sequester: One critical aspect of labile C (hydrochar) addition to soils is the feedback on the decomposition of native soil-C as priming (Keith *et al.*, 2011; Kuzyakov, 2010). Malghani *et al.* (2014) observed both, positive priming in the first 3 months after hydrochar application, and negative priming after the first 3 months.

For pyrochar, there are recent studies on char-C stability which supports findings in this study (Bamminger *et al.*, 2014; Kuzyakov *et al.*, 2014; Malghani *et al.*, 2013; Nguyen *et al.*, 2010; Zimmerman, 2010; Kuzyakov *et al.*, 2009). In addition to feedstock type, the char production temperature affects the differences in char-C degradability due to different degrees of aromatic C condensation which increased with increasing carbonization temperatures (Singh *et al.*, 2012; McBeath and Smernik, 2009). Pyrochar addition may also affect native soil-C and its decomposition via positive as well as negative priming (Fang *et al.*, 2014; Liu *et al.*, 2013; Lehmann and Joseph, 2009; Cheng *et al.*, 2006). Also pyrochars comprise a labile C pool mainly consisting of glycol and phospholipids which can be rapidly decomposed (Kuzyakov *et al.*, 2014). Around 0.3 – 1.0% of pyrochar can get lost via leaching as extractable soluble and colloidal fractions downwards the soil profile by 5 to 25 cm within two years e.g. with bioturbation or water percolation (Abiven *et al.*, 2011; Major *et al.*, 2010).

TO CONCLUDE, while pyrochar has a high potential for C-sequestration, faster mineralization of hydrochar compared to pyrochar showed their potential to act as a long-term fertilizer through slow nutrient release to soils. Moreover, the nutrient retention effect seems to be of very limited duration. After 7 months in the field, around 60 to 80% of the adsorption capacity of pyrochar was lost. The low stability of hydrochar with a higher proportion of functional groups and reactivity may offer such additional benefit. Plant available nutrients may be slowly released from hydrochar during its mineralization, wherefore hydrochar can be also used as slow-release fertilizer.

9.3 Reduction of NH_3 emissions from organic manure due to char application: functionality vs. economy *(Combining the results of the laboratory batch-experiments (Chapter 6) with the results of the laboratory incubation and adsorption-experiments from Chapter 7)*

The laboratory incubation experiment of Chapter 7 presented the results about amendment of manures with hydrochar or pyrochar to reduce NH_3 emissions from organic manures. The objectives of this study were to i) estimate the reduction potential of pyrochar and hydrochar on NH_3 emissions from organic manures and ii) investigate which char-mechanism (pH or adsorption) has more impact NH_3 volatilization.

A volatilization-diffusion experimental setup was used to conduct an incubation experiment under controlled conditions in a climate chamber with 10°C air temperature during a 4-week period. Cattle slurry and poultry litter were used as manure amendments and were mixed with either hydrochar or pyrochar. Sub-treatments with acid addition to the char/manure mixtures were conducted in order to differentiate an induced adsorption process of chars from a pH-effect through char addition on NH_3 volatilization. Treatments with soil were carried out in order to quantify the effect of either pyrochar or hydrochar on NH_3 volatilization from manure applied to soil. Furthermore, a sorption equilibrium experiment was conducted to determine the sorption equilibrium of NH_4^+ on chars' surface.

Hydrochar addition led to reduced NH_3 volatilization for both investigated manures due to its acidic pH (3.8) which implicates a stronger reduction-effect on manures' pH with hydrochars by shifting the $NH_3(aq)/NH_4^+$-equilibrium towards NH_4^+. The addition of pyrochars to both manures led to increase NH_3 emissions or showed no significant effect compared to pure manures. With regard to chars induced ph-effect, **hypothesis H_5** must be rejected. The result that hydrochar reduces NH_3 emissions whereby pyrochars increased it rejects **hypothesis H_6**. For manures, an imbalanced ratio between liming and adsorption towards stronger liming of manures, which results in a slight shift of the $NH_3(aq)/NH_4^+$-equilibrium towards NH_3 was suggested. Acidification to a pH of 5.5-5.8 reduced total NH_3 emissions by 50% to 70%. A lag time of 24 h was found before NH_3 starts to volatize assuming that in the first 24 h hours i) the addition of acid shifted the $NH_3(aq)/NH_4^+$-equilibrium towards 100% NH_4^+ (pH: 5.5) which significantly suppressed the NH_3-volatilization and afterwards ii) the acidity decreased by slight consumption of H^+ through urease which increased during urea hydrolysis to NH_3. Especially PL contains uric acid, which can be converted to urea by the enzyme uricase, and is in turn hydrolyzed to NH_3-N by the enzyme urease, thereby consuming H^+ ions and increasing pH during the process (Ferguson *et al.*, 1984).

Our observations showed no NH_4^+ adsorption of chars mixed with pure manure which contradicts findings from Chapter 6 where NH_4^+ adsorption of chars was found in a nutrient-solution. Both batch equilibrium media were different (nutrient solution *vs.* manures) which may result in blocked char binding sites with any organic material from manures inducing no adsorption. Hence our

results point out that the effects of char addition to manure on NH_3-emissions were almost exclusively driven by the char´s effect on pH. This is in accordance with findings by Mumme *et al.* (2014). For the tested chars, this suggests that the ability of chars to decrease N losses via NH_3 volatilization through adsorption is minor when the chars are applied directly to manure.

TO CONCLUDE, The effect of pyrochar and hydrochar produced from *Miscanthus* on NH_3 emissions from organic manure was mainly driven by char-induced pH changes. A reduction of NH_3 emissions due to adsorption of NH_4^+ especially to pyrochar was not observed. However, pH management of manure by char addition to reduce NH_3 emissions is rather ineffective as compared to direct acidification. To reach the same NH_3 reduction potential as acidification, a large, and therefore expensive, amount of char would be required. When char is added to acidified manures, the chars' contribution towards reducing NH_3 volatilization from manure was 10% of applied NH_4^+-N (up to 5% of the applied N_t). Therefore, based on our methods and observations, it can not be recommend to use either pyrochar or hydrochar to reduce NH_3 volatilization from organic manure.

9.4 Final Remarks: For which benefit do we want to use chars?

For pyrochar, an additional benefit regarding nutrient management or reduction of NH_3 emissions from organic manures was minor or not found. Chapter 6 showed that pyrochars lost their nutrient retention potential over the experimental time by up to 60-80%. When this loss occoured in the unvegetated or cover-crop period, most of the nutrients will rinse through soils into the groundwater or causes eutrophication of the receiving water bodies. Chapter 7 showed, that pyrochar could increase NH_3 emissions due to its liming effects on organic manures which shifts $NH_3(aq)/NH_4^+$-equilibrium towards NH_3. In Chapter 8, pyrochars were recommended for the usage as recalcitrant C-sequestration medium because they are stable against degradation. Summarizing, all three articles showed that the main benefit for soil amendment with especially pyrochar in the temperate zone is C-sequestration.

Hydrochars are very labile wherefore a usage as C-storage medium in soils is not recommended (Chapter 8). Nevertheless, due to its acid pH hydrochars may reduce NH_3 emissions by shifting the $NH_3(aq)/NH_4^+$-equilibrium towards NH_4^+. The higher proportion of functional groups and reactivity may offer such additional benefit. Plant available nutrients may be slowly released from hydrochar during its mineralization, wherefore hydrochar can be also used as slow-release fertilizer. However, both benefits were minor and the production of hydrochar is a very cost-consuming process so far.

Another big issue besides char-usage is the questions regarding the availability of biomass resources for char production as well as economic and greenhouse gas costs for its production and application. Without additional synergetic benefits of char application to agricultural soils char

application will not be adopted by farmers because they are expensive. For example, the netto costs including taxes for 1000 kg pyrochar is around 1200 € (NovoCarbo GmbH, Dörth, germany). Projected for an argricultural field scale application by 10 t ha^{-1}, the costs are 12,000 € ha^{-1}. The netto costs for hydrochar could not be assessed because the production is in an experimental stage and therefore they are not available at the marked. However, the acquisition cost for hydrohar used in the experiments of Chapter 6-8 was around 2,300 € per 100 kg hydrochar. Hence, soil amendment with hydrochar as slow-release fertilizer is more expensive as compared to mineral fertilizer by factor 40 to 100 (depending on fertilizer type, the costs are 22-52 € per 100 kg, (LWK-RP, 2015)) wherefore this usage is not recommend for economic reasons.

With regard to the increase of soil humus formation, especially pyrochars are not biologically active and could not substitute other biomasses such as straw or bark mulch wich are more active and cheaper. Futhermore, the production of pyrochar and/or hydrochar deprives biomasses from other systems such as forestry or agriculture which could affect humus degradation at other soil locations (Möller and Höpner, 2014). For example, in germany, most biomasses from, e.g., munincipal green waste and renewable ressources were used for composting or energetic conversion resulting in very litte amounts of residual materials for the production of chars. For example, 8% of the german electricity production originates from renewable resources, whereof an amount of 31% is from solid biomasses such as, e.g., wood (FNR, 2015). Moreover, 9% of the renewable resources are used for heat production, whereof the amount of all biogenic materials used for bioenergy reached 87% in 2014 (splitted in 64% from solid fuels; 11% gaseous fuels; 9% from biogenic wastes; 2% liquid fuels) (FNR, 2015). On a national scale such as for germany, the use of renewable resources to produce char for soil amendment may increase the competition between energy production and composting.

However, in this doctoral thesis the char application to soils showed no positive benefits besides C-sequestration for pyrochar on an economical or ecological scale. Therefore, one further question has to be asked: Why was char advertised as *panacea* for soil melioration in global research or public media? The amendment of agricultural soils with chars to improve yields was mostly investigated in tropical soils or in subtropical sandy soils where the soils are highly weathered, acidified as well as most of the nutrients were depleted (Lehmann and Rondon, 2006). Application of pyrochars to these soils induced positive impacts on soil fertility primarily due to its' liming effect by the high ash content on soils which improves significantly soils' CEC and AEC (Jeffery *et al.*, 2011; Lehmann and Joseph, 2009; Lehmann and Rondon, 2006). For sandy soils, the most important benefit is based on an increase in water holding capacity due to pyrochar application (Jeffery *et al.*, 2011). However, these benefits can not be adopt for all soils in the temperate zone exept for some

locations where soils with a high sand content occurs (e.g. Podzols). These soils could be ameliorate by the addition of pyrochar to increase pH or water holding capacity but this is expensive.

TO FINALLY CONCLUDE, hydrochar showed a minor multi-beneficial usage (slow release fertilizer or acidification medium to reduce NH_3 emissions) but are expensive and not available in an industrial scale. Therefore, it is not recommend to use hydrochar as soil amendment.

Based on Chapter 8, the main benefit due to the usage of pyrochar was C-sequestration but it is not recommend to use pyrochar to improve nutritient management in temperate zone agricultural soils. Confirmed by other studies, pyrochar could act as soil amendment to lime acidified soils. An application of pyrochar to improve water holding capacity may an appropriate amelioration of sandy soils.

With regard to climate-change and the necessity for irrigation in regions with sandy soils, future research should aim at biochemical interactions influencing soil-plant-water-root-nutrient interactions. Most studies were conducted in laboratory-experimental setups, therefore more long-term field scale experiments in 'real' agricultural environments needs to be further examined. With the focus on economy, costs of pyrochars should be strongly decreased to make the production and subsequent use more attractive for, e.g., municipalities or farmers who needs to ameliorate sandy soil sites.

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10 SUPPLEMENT

10.1 Supplement for Chapter 6

Table S1 Fitted parameters for the Freundlich and linear isotherm. Pyro750 = pyrochar; Hydro200, Hydro250 = hydrochar produced by 200, 250°C. Carbonized feedstocks are digestates (D), *Miscanthus* (M), woodchips (W). Level of significance are indicating by *** <0.0001; ** <0.001; * <0.01, · <0.05.

				Freundlich-Isotherm										Linear-Isotherm									
Soil	Ion	Treatment	Feed-stock	K_F	±	SE	Signf. Level	n	±	SE	Signf. Level	Residual std. error	R^2	a	±	SE	Signf. Level	Inter-cept (Y_0)	±	SE	Signf. Level	Residual std. error	R^2
Sandy loam	NO_3^-	Ctrl	-											0.01	±	0.0		-0.1	±	0.7		1.6	0.06
		Hydro200	D											0.0	±	0.0	***	-1.7	±	0.4	***	0.8	0.47
			M											0.0	±	0.0	*	-1.3	±	0.3	***	0.6	0.23
			W											0.0	±	0.0		-1.4	±	0.3	***	0.8	0.07
		Hydro250	D											0.0	±	0.0	***	-0.1	±	0.3		0.7	0.51
			M											0.0	±	0.0		-1.1	±	0.4	**	0.8	0.02
			W											0.0	±	0.0		-0.6	±	0.5		1.3	0.06
		Pyro750	D	0.9	±	0.4	*	1.8	±	0.4	***	1.6	0.71										
			M	1.1	±	0.3	***	1.5	±	0.1	***	1.5	0.95										
			W	2.5	±	0.3	***	1.8	±	0.1	***	1.4	0.94										
	NH_4^+	Ctrl	-	1.6	±	0.4	***	1.4	±	0.1	***	2.5	0.94										
		Hydro200	D	0.8	±	0.2	**	1.1	±	0.1	***	2.1	0.95										
			M	1.4	±	0.3	***	1.3	±	0.1	***	1.8	0.96										
			W	1.6	±	0.3	***	1.4	±	0.1	***	2.2	0.95										
		Hydro250	D	1.2	±	0.3	***	1.3	±	0.1	***	2.1	0.95										
			M	1.6	±	0.3	***	1.4	±	0.1	***	2.1	0.95										
			W	1.6	±	0.3	***	1.4	±	0.1	***	2.2	0.94										
		Pyro750	D	3.1	±	0.3	***	1.5	±	0.1	***	1.5	0.99										
			M	1.3	±	0.2	***	1.3	±	0.1	***	1.2	0.98										
			W	2.1	±	0.2	***	1.5	±	0.1	***	1.1	0.99										
	PO_4^{3-}	Ctrl	-											11.4	±	1.3	***	-22.3	±	4.3	***	6.0	0.82
		Hydro200	D											10.4	±	0.9	***	-33.4	±	3.8	***	4.4	0.89
			M											10.9	±	0.9	***	-26.4	±	3.4	***	4.3	0.89
			W											10.3	±	0.9	***	-25.6	±	3.5	***	4.6	0.88
		Hydro250	D											10.0	±	0.9	***	-31.7	±	3.7	***	4.4	0.89
			M											10.5	±	0.9	***	-22.0	±	3.1	***	4.4	0.89
			W											11.4	±	1.3	***	-22.0	±	4.1	***	5.7	0.82
		Pyro750	D											-6.1	±	0.6	***	59.1	±	9.4	***	13.0	0.86
			M											16.8	±	2.1	***	-22.5	±	5.2	***	6.9	0.78
			W											19.2	±	2.3	***	-5.1	±	3.4		6.7	0.80
	Ca^{2+}	Ctrl	-											0.0	±	0.0		-111.7	±	3.8	***	7.8	0.01
		Hydro200	D											0.2	±	0.0	***	-122.5	±	7.1	***	14.4	0.55
			M											0.0	±	0.1		-119.3	±	14.6	***	29.5	0.06
			W											0.0	±	0.1		-120.1	±	10.7	***	21.6	0.06
		Hydro250	D											0.1	±	0.1		-108.2	±	9.8	***	20.1	0.03
			M											0.1	±	0.0	*	-131.6	±	7.7	***	15.4	0.20
			W											0.1	±	0.0	**	-140.1	±	5.8	***	11.5	0.42
		Pyro750	D	5.7	±	2.3	*	1.3	±	0.1	***	38.1	0.91										
			M											0.3	±	0.1	***	-73.5	±	8.3	***	17.8	0.67
			W											0.1	±	0.1	.	-182.9	±	10.0	***	18.7	0.15
	Mg^{2+}	Ctrl	-											0.0	±	0.0		-11.4	±	0.5	***	1.1	0.08
		Hydro200	D											-0.5	±	0.0	***	-17.5	±	0.9	***	1.6	0.91
			M											-0.1	±	0.1		-11.6	±	1.6	***	3.4	0.30
			W											-0.1	±	0.1	.	-11.7	±	1.2	***	2.5	0.12

	Hydro250	D										-0.3	±	0.1	***	-19.3	±	1.6	***	3.0	0.51
		M										0.0	±	0.0		-12.7	±	0.9	***	1.9	0.03
		W										0.0	±	0.0		-13.7	±	0.5	***	1.0	0.04
	Pyro750	D										-1.5	±	0.0	***	-20.8	±	1.0	***	1.9	0.99
		M										-0.2	±	0.0	**	-10.0	±	1.0	***	2.0	0.41
		W										0.0	±	0.1		-13.4	±	1.2	***	2.4	0.05
K^+	Ctrl	-										0.7	±	0.1	***	-14.7	±	2.4	***	5.6	0.91
	Hydro200	D										0.5	±	0.1	***	-30.8	±	2.6	***	5.7	0.81
		M										0.5	±	0.1	***	-17.1	±	4.3	**	9.9	0.67
		W										0.6	±	0.1	***	-16.6	±	3.5	***	8.0	0.77
	Hydro250	D										0.4	±	0.1	***	-33.7	±	3.5	***	7.5	0.70
		M										0.6	±	0.1	***	-22.4	±	2.4	***	5.3	0.89
		W										0.6	±	0.1	***	-26.8	±	2.7	***	5.9	0.86
	Pyro750	D										-1.0	±	0.2	***	-442.1	±	55.7	***	68.1	0.49
		M										-0.6	±	0.1	***	-152.7	±	9.4	***	13.3	0.74
		W										0.3	±	0.0	***	-56.3	±	3.9	***	7.7	0.53
SO_4^{2-}	Ctrl	-										0.1	±	0.0	*	-15.8	±	0.7	***	1.4	0.19
	Hydro200	D										0.0	±	0.0		-15.5	±	0.6	***	1.3	0.06
		M										0.0	±	0.0		-15.1	±	0.6	***	1.2	0.04
		W										0.0	±	0.0		-15.4	±	0.5	***	1.0	0.05
	Hydro250	D										0.0	±	0.0	***	-13.8	±	0.2	***	0.5	0.49
		M										0.0	±	0.2		-14.8	±	0.8	***	0.9	0.03
		W										0.0	±	0.0		-14.7	±	0.6	***	1.2	0.02
	Pyro750	D										-0.1	±	0.0	**	-19.8	±	0.5	***	0.9	0.44
		M										0.0	±	0.0	.	-16.1	±	0.7	***	1.4	0.14
		W										0.0	±	0.0		-35.8	±	1.5	***	2.6	0.06

				Freundlich-Isotherm										**Linear-Isotherm**									
Soil	Ion	Treatment	Feed-stock	K_F	±	SE	Signf. Level	n	±	SE	Signf. Level	Residual std. error	R^2	a	±	SE	Signf. Level	Inter-cept (Y_0)	±	SE	Signf. Level	Residual std. error	R^2
Loamy sand	NO_3^-	Ctrl	-											-0.01	±	0.0		-11.5	±	0.8	***	1.8	0.06
		Hydro200	D											0.073	±	0.0	**	-13.1	±	0.8	***	1.8	0.36
			M											0.050	±	0.0	*	-13.5	±	0.6	***	1.4	0.29
			W											0.028	±	0.0		-13.1	±	0.8	***	1.7	0.04
		Hydro250	D											0.052	±	0.0	.	-12.6	±	1.1	***	2.3	0.11
			M											0.056	±	0.0	*	-13.8	±	0.9	***	1.9	0.21
			W											0.019	±	0.0		-12.5	±	0.7	***	1.5	0.00
		Pyro750	D											0.133	±	0.0	***	-10.5	±	0.7	***	1.6	0.72
			M											0.256	±	0.0	***	-11.3	±	0.9	***	2.0	0.85
			W											0.308	±	0.0	***	-7.9	±	1.1	***	2.4	0.84
	NH_4^+	Ctrl	-	7.8	±	0.6	***	1.6	±	0.1	***	2.8	0.99										
		Hydro200	D	6.4	±	0.4	***	1.5	±	0.0	***	2.2	0.99										
			M	8.5	±	1.0	***	1.6	±	0.1	***	4.6	0.97										
			W	8.4	±	1.1	***	1.6	±	0.1	***	4.5	0.96										
		Hydro250	D	8.2	±	0.8	***	1.6	±	0.1	***	3.5	0.98										
			M	9.2	±	0.9	***	1.6	±	0.1	***	3.9	0.98										
			W	9.0	±	0.8	***	1.6	±	0.1	***	3.6	0.98										
		Pyro750	D	5.3	±	0.9	***	1.3	±	0.1	***	5.5	0.96										
			M	5.0	±	0.3	***	1.4	±	0.0	***	1.6	1.00										
			W	6.7	±	0.3	***	1.5	±	0.0	***	1.6	1.00										
	PO_4^{3-}	Ctrl	-											16.6	±	2.5	***	-11.8	±	5.0	*	8.4	0.72
		Hydro200	D											16.9	±	1.3	***	-20.5	±	3.1	***	4.4	0.91
			M											16.7	±	2.7	***	-11.6	±	5.5	.	8.7	0.69
			W											15.8	±	2.7	***	-10.9	±	5.6	.	9.0	0.67

	Hydro250	D	17.1	±	2.3	***	-20.1	±	5.3	**	7.6	0.76
		M	16.5	±	2.4	***	-11.5	±	4.8	*	8.1	0.73
		W	16.9	±	2.5	***	-11.5	±	5.0	*	8.3	0.72
	Pyro750	D	-7.0	±	1.0	***	52.1	±	9.1	***	14.8	0.74
		M	17.7	±	1.8	***	-20.3	±	4.1	***	6.0	0.85
		W	19.3	±	2.1	***	-8.5	±	3.5	*	6.6	0.82
Ca^{2+}	Ctrl	-	-0.3	±	0.1	**	-204.1	±	18.1	***	33.5	0.33
	Hydro200	D	-0.3	±	0.0	***	-198.7	±	8.3	***	15.3	0.82
		M	-0.2	±	0.1	***	-210.7	±	12.5	***	22.7	0.49
		W	-0.3	±	0.1	***	-197.1	±	12.7	***	23.5	0.65
	Hydro250	D	-0.1	±	0.1	.	-224.1	±	18.4	***	32.8	0.11
		M	-0.2	±	0.1	*	-227.2	±	16.8	***	29.9	0.18
		W	-0.3	±	0.1	**	-217.4	±	18.0	***	32.3	0.35
	Pyro750	D					NA					
		M	-0.2	±	0.0	***	-182.4	±	6.2	***	11.6	0.73
		W	-0.2	±	0.0	***	-240.6	±	4.5	***	8.2	0.88
Mg^{2+}	Ctrl	-	0.537	±	0.1	***	-11.1	±	1.2	***	2.6	0.76
	Hydro200	D	-0.086	±	0.1		-16.2	±	1.4	***	2.8	0.04
		M	0.421	±	0.1	***	-12.7	±	1.2	***	2.4	0.71
		W	0.329	±	0.5	***	-11.8	±	1.0	***	2.0	0.69
	Hydro250	D	0.180	±	0.1	**	-16.0	±	1.1	***	2.1	0.38
		M	0.489	±	0.1	***	-13.7	±	1.2	***	2.5	0.73
		W	0.464	±	0.1	***	-12.8	±	1.2	***	2.6	0.70
	Pyro750	D	-0.863	±	0.1	***	-18.2	±	3.9	***	7.4	0.67
		M	0.354	±	0.0	***	-11.3	±	0.8	***	1.7	0.78
		W	0.276	±	0.1	*	-11.1	±	1.8	***	3.7	0.29
K^{+}	Ctrl	-	1.300	±	0.1	***	-40.4	±	4.3	***	8.9	0.91
	Hydro200	D	1.022	±	0.1	***	-55.1	±	4.6	***	8.9	0.88
		M	1.176	±	0.1	***	-41.5	±	4.6	***	9.3	0.89
		W	1.179	±	0.1	***	-40.0	±	3.2	***	6.6	0.94
	Hydro250	D	0.958	±	0.1	***	-53.3	±	6.0	***	11.7	0.79
		M	1.198	±	0.1	***	-48.0	±	4.4	***	8.9	0.90
		W	1.095	±	0.1	***	-47.4	±	5.0	***	10.0	0.86
	Pyro750	D	-0.925	±	0.3	**	-388.3	±	57.4	***	44.5	0.34
		M	-0.245	±	0.1	*	-128.8	±	7.2	***	11.0	0.30
		W	0.722	±	0.1	***	-69.1	±	5.3	***	9.9	0.77
SO_4^{2-}	Ctrl	-	0.2	±	0.1		-18.7	±	2.8	***	5.7	0.06
	Hydro200	D	1.1	±	0.7		-416.3	±	19.2	***	38.6	0.07
		M	4.2	±	2.4	.	-387.6	±	63.8	***	129.0	0.11
		W	3.6	±	2.5		-374.3	±	65.9	***	134.0	0.06
	Hydro250	D	3.8	±	2.4		-360.9	±	61.9	***	126.5	0.09
		M	4.0	±	2.2	.	-385.5	±	58.4	***	118.2	0.12
		W	2.6	±	2.2		-351.1	±	59.2	***	121.6	0.02
	Pyro750	D	5.5	±	2.2	*	-597.3	±	61.7	***	115.2	0.23
		M	0.2	±	0.7		-422.8	±	19.7	***	39.6	0.06
		W	-0.3	±	0.8		-806.3	±	26.1	***	45.3	0.68

Table S2 pH-Values for every batch-solution concentration and treatment for the laboratory experiment.

Experiment	Soil type	Feedstock	Char type	°C	pH ($CaCl_2$)					
					P1	P2	P3	P4	P5	P6
Lab	Sandy loam	Digestates	Hydrochar	200	6.3	6.1	5.8	5.6	6.0	5.7
			Hydrochar	250	6.3	5.9	5.7	5.7	5.8	5.6
			Pyrochar	750	7.6	7.2	6.9	6.7	7.0	6.5
		Miscanthus	Hydrochar	200	6.1	5.8	5.8	5.5	5.7	5.5
			Hydrochar	250	6.1	6.0	5.7	5.5	5.8	5.5
			Pyrochar	750	6.9	6.7	6.5	6.3	6.5	6.5
		Woodchips	Hydrochar	200	6.1	5.8	5.6	5.4	5.7	5.4
			Hydrochar	250	6.2	5.9	5.7	5.5	5.8	5.6
			Pyrochar	750	7.0	6.8	6.8	6.5	6.7	6.4
		Ctrl (pure soil)	-	-	6.1	5.8	5.7	5.7	5.7	5.6
	Silty loam	Digestates	Hydrochar	200	7.1	6.9	6.7	6.7	6.6	6.7
			Hydrochar	250	7.1	7.0	6.7	6.7	6.5	6.7
			Pyrochar	750	7.9	7.7	7.4	7.4	7.1	7.3
		Miscanthus	Hydrochar	200	7.1	6.8	6.7	6.7	6.5	6.7
			Hydrochar	250	7.1	7.0	6.7	6.7	6.5	6.6
			Pyrochar	750	7.3	7.2	7.0	7.0	6.9	6.9
		Woodchips	Hydrochar	200	7.0	6.7	6.6	6.6	6.4	6.5
			Hydrochar	250	7.0	6.9	6.8	6.7	6.5	6.6
			Pyrochar	750	7.3	7.3	7.0	7.0	6.9	7.0
		Ctrl (pure soil)	-	-	7	6.9	6.7	6.7	6.4	6.6

.

Table S3 Adjusted p-values for statistical comparisons between feedstocks within one char type (e.g. d : m = char from digestates to char from *Miscanthus*); control soil to feedstock within one char type (e.g. Ctrl : d = control soil to char from digestates); and same feedstock to different char types (e.g. Pyro750-d : Hydro200-d = pyrochar from digestates to Hydro200 from digestates) for each ion. * Statistical comparison was made with GAM (general additive model). Significant differences were assumed by $p \leq 0.05$.

		Sandy loam							Silty loam						
		NO_3^-	NH_4^+	PO_4^{3-}	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	NO_3^-	NH_4^+	PO_4^{3-}	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+
Pyrochars	d : m	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	d : w	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	m : w	<0.01	0.03	<0.01	<0.01	<0.01	0.24	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05	<0.01
	Ctrl : d	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01*	<0.01	<0.01
	Ctrl : m	<0.01	0.10	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	0.11	<0.01	<0.01*	<0.01	<0.01
	Ctrl : w	<0.01	0.02	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	0.01	0.10	<0.01	<0.01*	<0.01	<0.01
	Pyro750-d : Hydro200-d	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01*	<0.01	<0.01
	Pyro750-m : Hydro200-m	<0.01	0.23	<0.01	<0.01	<0.01	0.29	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01*	0.43	<0.01
	Pyro750-w : Hydro200-w	<0.01	0.17	<0.01	<0.01	<0.01	0.74	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01*	0.90	<0.01
	Pyro750-d : Hydro250-d	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.09	<0.01	<0.01	<0.01*	<0.01	<0.01
	Pyro750-m : Hydro250-m	<0.01	0.18	<0.01	<0.01	0.03	0.29	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01*	0.24	<0.01
	Pyro750-w : Hydro250-w	<0.01	0.01	<0.01	<0.01	0.01	0.06	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01*	0.21	<0.01
Hydro200	d : m	0.33	0.98	<0.01	0.76	<0.01	0.00	<0.01	0.29	<0.01	0.02	<0.01	0.62	<0.01	<0.01
	d : w	0.32	0.98	0.01	0.76	<0.01	<0.01	<0.01	0.29	<0.01	0.02	<0.01	0.62	<0.01	<0.01
	m : w	0.53	0.98	0.81	0.76	0.64	0.63	0.77	0.67	0.93	0.95	0.98	0.68	0.51	0.53
	Ctrl : d	0.05	0.65	<0.01	0.32	<0.01	<0.01	<0.01	0.43	0.37	0.03	<0.01	0.14	0.51	<0.01
	Ctrl : m	0.03	0.65	0.04	0.44	<0.01	0.03	<0.01	0.43	<0.01	0.99	<0.01	0.50	0.18	0.45
	Ctrl : w	0.03	0.65	0.03	0.32	<0.01	0.02	<0.01	0.50	0.02	0.99	<0.01	0.50	<0.01	0.45
	Hydro200-d : Pyro750-d	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01*	<0.01	<0.01
	Hydro200-m : Pyro750-m	<0.01	0.23	<0.01	<0.01	<0.01	0.29	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01*	0.43	<0.01
	Hydro200-w : Pyro750-w	<0.01	0.17	<0.01	<0.01	<0.01	0.74	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01*	0.90	<0.01
	Hydro200-d : Hydro250-d	<0.01	0.61	0.02	<0.01	0.23	0.02	0.35	0.66	<0.01	0.28	<0.01	0.02	<0.01	0.83
	Hydro200-m : Hydro250-m	0.06	0.83	0.27	0.48	0.12	0.29	0.11	0.65	0.58	0.97	0.78	0.60	0.59	<0.01
	Hydro200-w : Hydro250-w	0.11	0.88	0.97	0.73	0.01	0.04	0.02	0.79	0.56	0.88	0.99	0.49	0.03	<0.01
Hydro250	d : m	0.33	0.21	<0.01	0.11	<0.01	<0.01	<0.01	0.46	0.14	0.22	0.94	0.68	<0.01	0.02
	d : w	0.33	0.21	<0.01	0.08	<0.01	<0.01	<0.01	0.46	0.40	0.22	0.94	0.68	<0.01	0.09
	m : w	0.33	0.75	0.36	0.67	0.45	0.15	0.25	0.46	0.54	0.98	0.94	0.68	0.88	0.56
	Ctrl : d	<0.01	0.15	<0.01	0.00	0.01	<0.01	<0.01	0.53	0.03	0.49	<0.01	0.78	<0.01	<0.01
	Ctrl : m	0.02	0.68	0.49	0.08	0.03	0.07	<0.01	0.53	0.03	0.99	<0.01	0.78	0.03	0.05
	Ctrl : w	0.11	0.86	0.98	0.15	0.01	0.03	<0.01	0.63	0.03	0.99	<0.01	0.78	0.04	0.01
	Hydro250-d : Hydro200-d	<0.01	0.61	0.02	<0.01	0.23	0.02	0.35	0.66	<0.01	0.28	<0.01	0.02	<0.01	0.83
	Hydro250-m : Hydro200-m	0.06	0.83	0.27	0.48	0.12	0.29	0.11	0.65	0.58	0.97	0.78	0.60	0.59	<0.01
	Hydro250-w : Hydro200-w	0.11	0.88	0.97	0.73	0.01	0.04	0.02	0.79	0.56	0.88	0.99	0.49	0.03	<0.01
	Hydro250-d : Pyro750-d	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.09	<0.01	<0.01	<0.01*	<0.01	<0.01
	Hydro250-m : Pyro750-m	<0.01	0.18	<0.01	<0.01	0.03	0.29	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01*	0.24	<0.01
	Hydro250-w : Pyro750-w	<0.01	0.01	<0.01	<0.01	0.01	0.06	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01*	0.21	<0.01

Table S4 Adjusted p-values for statistical comparisons of same char type and same feedstock between sandy and loamy soil for each ion. * Statistical comparison was made with GAM (general additive model). Significant differences were assumed by $p \leq 0.05$.

	Sandy loam vs. Silty loam						
	NO_3^-	NH_4^+	PO_4^{3-}	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+
Ctrl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pyro750-D	<0.01	<0.01	0.11	<0.01	<0.01*	<0.01	0.03
Pyro750-M	<0.01	<0.01	0.34	<0.01	<0.01	<0.01	<0.01
Pyro750-W	<0.01	<0.01	0.55	<0.01	<0.01	<0.01	<0.01
Hydro250-D	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Hydro250-M	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Hydro250-W	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Hydro200-D	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Hydro200-M	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Hydro200-W	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Table S5 Fitted parameters for the Freundlich and linear isotherm of fresh (T0) and aged chars (T1). Pyro750 = pyrochar; Hydro200 =hydrochar produced by 200°C. Carbonized feedstocks are only *Miscanthus*. Sites are: 1= Bortfeld, 2=Querenhorst, 3=Volkmarsdorf. Level of significance are indicating by *** <0.0001; ** <0.001; * <0.01, · <0.05.

				Freundlich-Isotherm										Linear-Isotherm									
Sampling Time	Ion	Treat-ment	Site	KF	±	SE	Signif. Level	n	±	SE	Signif. Level	Residual std. error	R^2	a	±	SE	Signif. Level	Intercept (Y_0)	±	SE	Signif. Level	Residual std. error	R^2
T_0	NO_3^-	Ctrl	1		±				±					-0.58	±	0.1		-24.22	±	3.3	***	6.57	<0.01
			2		±				±					-0.28	±	0.0	**	-7.98	±	1.0	***	2.34	0.44
			3		±				±					-0.65	±	0.1		-21.95	±	5.0	***	10.17	0.09
		Pyro750	1		±				±					-0.24	±	0.1	*	-11.58	±	2.3	*	1.12	0.25
			2		±				±					-0.25	±	0.0	***	-3.58	±	2.3	***	1.14	0.85
			3		±				±					-0.36	±	0.1		-15.84	±	2.4	**	1.05	0.09
		Hydro200	1		±				±					0.06	±	0.0		-11.58	±	2.2	***	4.99	0.03
			2		±				±					-0.20	±	0.0		-3.58	±	2.3		5.47	0.31
			3		±				±					0.02	±	0.1		-15.84	±	2.4	***	5.09	0.01
	NH_4^+	Ctrl	1	3.49	±	0.4	***	1.40	±	0.1	***	1.71	0.96		±				±				
			2	5.42	±	0.8	***	2.02	±	0.2	***	2.78	0.93		±				±				
			3	4.16	±	0.5	***	1.85	±	0.1	***	1.91	0.96		±				±				
		Pyro750	1	7.99	±	0.6	***	2.24	±	0.1	***	1.96	0.97		±				±				
			2	5.63	±	0.5	***	2.06	±	0.1	***	1.76	0.97		±				±				
			3	8.30	±	1.1	***	2.29	±	0.2	***	1.74	0.97		±				±				
		Hydro200	1	4.15	±	0.4	***	1.70	±	0.1	***	1.92	0.97		±				±				
			2	6.64	±	0.5	***	2.28	±	0.1	***	1.82	0.97		±				±				
			3	4.10	±	0.4	***	1.73	±	0.1	***	3.66	0.92		±				±				
	PO_4^{3-}	Ctrl	1		±				±					21.15	±	1.8	***	-18.70	±	3.5	***	5.07	0.89
			2		±				±					18.45	±	2.7	***	-27.36	±	6.9	**	8.52	0.74
			3		±				±					23.31	±	2.3	***	-14.37	±	3.7	**	5.84	0.86
		Pyro750	1		±				±					25.01	±	4.6	***	-31.24	±	9.4	***	4.72	0.91
			2		±				±					9.14	±	2.1	***	-7.08	±	6.0	*	6.77	0.81
			3		±				±					27.03	±	2.6	***	-25.33	±	4.5	***	4.48	0.91
		Hydro200	1		±				±					23.33	±	1.8	***	-23.46	±	3.5	**	9.75	0.65
			2		±				±					12.27	±	1.5	***	-10.25	±	3.8		10.55	0.54
			3		±				±					19.73	±	1.5	***	-11.21	±	2.6	***	5.71	0.87
	Ca^{2+}	Ctrl	1		±				±					-0.24	±	0.1		-41.22	±	15.2	*	33.60	<0.01
			2		±				±					-0.09	±	0.0	**	-45.54	±	6.2	***	13.74	0.48
			3		±				±					-0.40	±	0.1		-56.70	±	14.5	**	31.60	0.13
		Pyro750	1		±				±					0.29	±	0.1		17.12	±	13.9	*	27.00	0.04
			2		±				±					0.12	±	0.0	**	-9.80	±	10.2	***	10.44	0.36
			3		±				±					-0.01	±	0.0		-13.02	±	10.6	***	28.84	0.08
		Hydro200	1		±				±					-0.12	±	0.0	.	-33.89	±	12.1		33.25	0.21
			2		±				±					-0.11	±	0.0	*	-37.98	±	4.6		23.69	0.31
			3		±				±					-0.40	±	0.1		-64.74	±	13.4		24.49	0.05
	Mg^{2+}	Ctrl	1		±				±					-0.05	±	0.1		-5.24	±	2.3	***	3.15	<0.01
			2		±				±					-0.08	±	0.1		-7.26	±	1.5	***	3.17	0.07
			3		±				±					-0.01	±	0.1		-6.72	±	1.4	***	3.15	0.03
		Pyro750	1		±				±					-0.18	±	0.1	*	-2.75	±	1.5	.	3.49	0.24
			2		±				±					0.04	±	0.1		-2.79	±	1.0	*	2.24	0.03
			3		±				±					-0.08	±	0.1		-4.46	±	1.1	***	2.37	0.13
		Hydro200	1		±				±					-0.04	±	0.1		-4.99	±	2.2	*	4.82	0.01
			2		±				±					-0.20	±	0.1	.	-6.88	±	2.0	**	4.41	0.21
			3		±				±					0.07	±	0.1		-6.40	±	1.1	**	3.92	0.04
	K^+	Ctrl	1		±				±					-0.45	±	0.1	**	-49.12	±	4.8	***	9.31	0.45
			2		±				±					-0.93	±	0.2	.	-45.84	±	23.3		44.34	0.06
			3		±				±					-0.16	±	0.1	.	-25.72	±	13.5		27.77	0.06
		Pyro750	1		±				±					-2.13	±	0.1	***	-172.96	±	16.5	***	16.46	0.58
			2		±				±					-1.03	±	0.1		-82.88	±	10.4	***	18.16	<0.01
			3		±				±					-1.84	±	0.1	***	-158.92	±	7.2	***	9.71	0.51
		Hydro200	1		±				±					0.25	±	0.1	*	-52.39	±	5.7	***	10.82	0.30
			2		±				±					-0.01	±	0.2		-59.17	±	13.7	***	25.87	<0.01
			3		±				±					0.60	±	0.0	***	-26.92	±	2.2	***	4.61	0.92
	SO_4^{2-}	Ctrl	1		±				±					-0.03	±	0.0	.	-1.47	±	0.3	***	0.78	0.16
			2		±				±					0.10	±	0.1		-10.91	±	3.5	**	7.35	0.03
			3		±				±					-0.05	±	0.0	.	-0.78	±	0.6		1.29	0.21
		Pyro750	1		±				±					-0.03	±	0.0		-4.09	±	0.5	***	1.16	0.13
			2		±				±					0.19	±	0.1	**	-6.10	±	1.4	***	3.19	0.39
			3		±				±					-0.02	±	0.0		-3.28	±	0.4	***	0.97	0.05
		Hydro200	1		±				±					0.03	±	0.0		-0.45	±	0.4		0.94	0.16
			2		±				±					0.19	±	0.0	***	-5.90	±	0.7	***	1.48	0.73
			3		±				±					-0.01	±	0.0		0.14	±	0.3		0.77	0.06

				Freundlich-Isotherm										Linear-Isotherm									
Sampling Time	Ion	Treatment	Site	KF	±	SE	Signif. Level	n	±	SE	Signif. Level	Residual std. error	R^2	a	±	SE	Signif. Level	Intercept (Y_0)	±	SE	Signif. Level	Residual std. error	adj R^2
T_1	NO_3^-	Ctrl	1		±				±					-0.28	±	0.0	***	-4.37	±	1.1	**	2.66	0.68
			2		±				±					-0.66	±	0.1		-23.61	±	4.1	***	8.28	0.08
			3		±				±					-0.37	±	0.0	**	-9.05	±	2.2	***	5.02	0.35
		Pyro750	1		±				±					-0.36	±	0.1		-11.78	±	2.2	***	4.86	0.14
			2		±				±					-0.43	±	0.1		-16.04	±	4.2	**	8.89	0.01
			3		±				±					-0.40	±	0.1		-13.17	±	2.7	***	6.15	0.13
		Hydro200	1		±				±					-0.30	±	0.0	***	-5.38	±	0.8	***	1.80	0.82
			2		±				±					-0.01	±	0.0		1.69	±	0.4	**	1.01	0.07
			3		±				±					-0.18	±	0.0	***	-5.45	±	0.8	***	1.93	0.80
	NH_4^+	Ctrl	1	5.15	±	0.6	***	1.95	±	0.1	***	2.30	0.95		±				±				
			2	6.26	±	0.7	***	1.72	±	0.1	***	3.22	0.96		±				±				
			3	7.61	±	0.4	***	1.86	±	0.1	***	1.46	0.99		±				±				
		Pyro750	1	3.57	±	0.3	***	1.58	±	0.1	***	1.53	0.98		±				±				
			2	5.87	±	0.5	***	1.64	±	0.1	***	2.42	0.98		±				±				
			3	8.13	±	0.4	***	1.88	±	0.1	***	1.48	0.99		±				±				
		Hydro200	1	4.70	±	0.4	***	1.89	±	0.1	***	1.62	0.98		±				±				
			2	8.15	±	0.4	***	1.80	±	0.1	***	1.75	0.99		±				±				
			3	8.65	±	0.4	***	1.87	±	0.0	***	1.54	0.99		±				±				
	PO_4^{3-}	Ctrl	1	8.85	±	2.0	***	0.94	±	0.9	***	8.35	0.73		±				±				
			2	19.27	±	0.9	***	0.63	±	0.6	***	3.10	0.96		±				±				
			3	17.79	±	1.8	***	0.84	±	0.8	***	6.51	0.86		±				±				
		Pyro750	1	4.82	±	1.4	**	0.61	±	0.6	***	7.35	0.79		±				±				
			2	11.02	±	1.5	***	0.51	±	0.5	***	5.20	0.90		±				±				
			3	14.88	±	1.8	***	0.76	±	0.8	***	6.76	0.84		±				±				
		Hydro200	1	8.99	±	1.9	***	0.86	±	0.9	***	7.65	0.76		±				±				
			2	17.93	±	1.1	***	0.67	±	0.7	***	3.47	0.95		±				±				
			3	21.13	±	1.7	***	0.86	±	0.9	***	6.32	0.87		±				±				
	Ca^{2+}	Ctrl	1		±				±					0.05	±	0.1		-63.16	±	11.8	***	25.70	0.33
			2		±				±					-0.05	±	0.0		-91.15	±	8.1	***	16.93	0.08
			3		±				±					0.00	±	0.0		-72.50	±	5.2	***	11.26	<0.01
		Pyro750	1		±				±					-0.01	±	0.0		-97.45	±	7.6	***	15.80	<0.01
			2		±				±					0.01	±	0.0		-46.66	±	8.5	***	18.77	<0.01
			3		±				±					-0.05	±	0.0	*	-66.36	±	3.8	***	8.30	0.24
		Hydro200	1		±				±					0.04	±	0.1		-61.33	±	10.7	***	23.27	0.03
			2		±				±					-0.05	±	0.0		-77.71	±	6.0	***	12.69	0.11
			3		±				±					-0.06	±	0.0		-59.91	±	6.4	***	14.00	0.15
	Mg^{2+}	Ctrl	1		±				±					0.13	±	0.1	.	-4.17	±	1.2	**	2.72	0.18
			2		±				±					-0.56	±	0.1	***	-13.12	±	2.9	***	5.84	0.57
			3		±				±					-0.42	±	0.0	***	-10.80	±	0.7	***	1.43	0.92
		Pyro750	1		±				±					-0.09	±	0.1		-9.26	±	2.1	***	4.44	0.04
			2		±				±					-0.48	±	0.0	***	-9.89	±	0.9	***	1.84	0.91
			3		±				±					-0.48	±	0.1	***	-10.20	±	2.1	***	4.42	0.63
		Hydro200	1		±				±					0.00	±	0.1		-5.71	±	1.3	***	2.83	<0.01
			2		±				±					-0.56	±	0.1	***	-13.80	±	1.8	***	3.64	0.78
			3		±				±					-0.55	±	0.0	***	-10.40	±	0.7	***	1.55	0.95
	K^+	Ctrl	1		±				±					-0.11	±	0.3		-24.06	±	19.9		41.60	<0.01
			2		±				±					0.68	±	0.2	*	-28.87	±	12.1	*	24.69	0.33
			3		±				±					0.58	±	0.2	*	-41.89	±	11.2	**	22.51	0.33
		Pyro750	1		±				±					-0.39	±	0.4		-10.45	±	26.8		56.52	0.05
			2		±				±					-1.29	±	0.4	**	-64.78	±	39.7		62.76	0.39
			3		±				±					0.46	±	0.3		-32.39	±	15.3	.	31.61	0.14
		Hydro200	1		±				±					-0.74	±	0.4		-7.57	±	27.9		59.06	0.16
			2		±				±					0.59	±	0.2	*	-32.47	±	10.8	**	21.98	0.33
			3		±				±					0.65	±	0.2	**	-43.18	±	10.3	***	20.71	0.41
	SO_4^{2-}	Ctrl	1		±				±					0.17	±	0.0	***	-4.44	±	0.3	***	0.72	0.91
			2		±				±					-0.08	±	0.1		-7.56	±	1.8	***	3.83	0.07
			3		±				±					0.16	±	0.0	***	-6.63	±	0.5	***	1.19	0.76
		Pyro750	1		±				±					0.14	±	0.1	*	-7.88	±	1.5	***	3.41	0.24
			2		±				±					-0.11	±	0.1		-8.96	±	3.0	**	6.27	0.06
			3		±				±					0.20	±	0.0	***	-7.45	±	1.0	***	2.29	0.56
		Hydro200	1		±				±					0.13	±	0.0	***	-4.41	±	0.7	***	1.68	0.53
			2		±				±					-0.03	±	0.1		-7.86	±	1.8	***	3.88	<0.01
			3		±				±					0.12	±	0.0	**	-7.10	±	0.8	***	1.69	0.49

Table S6 pH-Values for every batch-solution concentration and treatment for the field experiment. Carbonized feedstocks are only *Miscanthus*.

Sampling Time	Site	Char type	°C	pH ($CaCl_2$)					
				P1	P2	P3	P4	P5	P6
T_0	1 Bortfeld (sandy loam)	Hydrochar	200	6.0	6.4	6.3	6.2	6.1	6.1
		Pyrochar	750	6.7	6.9	6.9	6.7	6.7	6.6
		Ctrl (pure soil)		6.1	6.5	6.4	6.3	6.3	6.2
	2 Querenhorst (loamy sand)	Hydrochar	200	6.3	6.6	6.6	6.4	6.4	6.3
		Pyrochar	750	6.8	6.7	7.1	6.9	6.9	6.8
		Ctrl (pure soil)		6.4	6.8	6.8	6.6	6.6	6.5
	3 Volkmarsdorf (sandy loam)	Hydrochar	200	6.6	6.7	6.7	6.6	6.5	6.5
		Pyrochar	750	6.4	7.3	7.3	7.2	7.1	7.1
		Ctrl (pure soil)		7.0	6.9	7.0	6.7	6.7	6.7
T_1	1 Bortfeld (sandy loam)	Hydrochar	200	6.5	6.4	6.3	6.1	6.1	6.0
		Pyrochar	750	6.5	6.2	6.2	6.0	6.0	5.9
		Ctrl (pure soil)		6.7	6.6	6.6	6.4	6.0	6.3
	2 Querenhorst (loamy sand)	Hydrochar	200	6.7	6.6	6.5	6.4	6.3	6.3
		Pyrochar	750	6.9	6.8	6.8	6.6	6.5	6.5
		Ctrl (pure soil)		6.6	6.5	6.5	6.3	6.5	6.3
	3 Volkmarsdorf (sandy loam)	Hydrochar	200	6.6	6.6	6.5	6.4	6.4	6.3
		Pyrochar	750	6.9	6.8	6.8	6.5	6.6	6.6
		Ctrl (pure soil)		6.7	6.6	6.6	6.5	6.6	6.4

Table S7 Adjusted p-values for statistical comparisons of the field incubation between char type (Pyro750 vs. Hydro200) and char type to control (Ctrl) for each ion and sampling time (T_0 & T_1).

Site		T_0							T_1						
		NO_3^-	NH_4^+	PO_4^{3-}	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	NO_3^-	NH_4^+	PO_4^{3-}	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+
1 Bortfeld (sandy loam)	Pyro750 : Hydro200	<0.01	<0.01	0.14	<0.01	<0.01	1	<0.01	<0.01	0.04	1	<0.05	<0.01	<0.05	1
	Ctrl : Pyro750	<0.01	<0.01	0.15	<0.01	<0.01	1	<0.01	<0.05	0.13	0.88	<0.01	<0.01	<0.01	1
	Ctrl : Hydro200	<0.01	<0.01	1	<0.01	0.70	1	1	0.91	1	1	0.05	1	0.08	0.92
2 Querenhorst (loamy sand)	Pyro750 : Hydro200	<0.01	1	0.49	0.26	<0.01	<0.01	0.24	<0.01	<0.01	<0.05	0.45	<0.01	<0.01	<0.01
	Ctrl : Pyro750	0.06	0.73	0.38	<0.01	<0.01	<0.01	0.06	0.14	1	<0.01	0.67	<0.01	<0.01	<0.01
	Ctrl : Hydro200	<0.01	1	0.61	<0.01	1	0.91	0.68	<0.01	<0.01	0.46	1	0.24	1	1
3 Volkmarsdorf (sandy loam)	Pyro750 : Hydro200	<0.01	<0.01	0.30	<0.01	<0.01	0.49	<0.01	<0.01	<0.01	0.22	0.53	0.61	<0.05	1
	Ctrl : Pyro750	<0.01	<0.05	0.41	0.12	<0.01	1	<0.01	1	0.27	1	0.43	1	<0.05	1
	Ctrl : Hydro200	<0.01	<0.01	0.87	<0.01	1	1	<0.01	<0.05	<0.01	1	0.27	1	<0.05	1

Table S8 Adjusted p-values for statistical comparisons of two sampling times (T_0 & T_1) of field incubated chars. Comparisions are for same char type or control each ion. * Statistical comparison was made with GAM (general additive model). Significant differences were assumed by $p \leq 0.05$.

Site		T_0 vs. T_1						
		NO_3^-	NH_4^+	PO_4^{3-}	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+
1 Bortfeld (sandy loam)	Ctrl	<0.01	<0.01	<0.01*	<0.01	0.48	<0.05	<0.01
	Pyro750	<0.01	0.52	<0.01*	<0.01	<0.01	<0.05	<0.01
	Hydro200	0.09	<0.01	<0.01*	<0.01	<0.05	0.28	<0.01
2 Querenhorst (loamy sand)	Ctrl	<0.01	<0.01	<0.01*	0.11	<0.01	<0.01	<0.01
	Pyro750	<0.01	<0.01	<0.01*	<0.01	<0.01	<0.01	<0.01
	Hydro200	<0.05	<0.01	<0.01*	<0.01	<0.01	<0.01	<0.01
3 Volkmarsdorf (sandy loam)	Ctrl	<0.01	<0.01	<0.01*	<0.01	<0.01	<0.01	0.61
	Pyro750	<0.01	<0.01	<0.01*	<0.01	<0.01	<0.01	<0.01
	Hydro200	0.45	<0.01	<0.01*	<0.01	0.07	<0.01	<0.01

10.2 Supplement for Chapter 7

Table S1 Multifactorial ANOVA about significant influences of tested treatment factors on the saturation curves' asymptote (*A*) and the exponential decay constant (κ).

Factor	DF	*F*-value	*p*-value
A: Intercept	1	21,052	<0.0001
A: Manure type	1	24.6	<0.0001
A: Soil	1	6,863	<0.0001
A: Char type	2	33.2	<0.0001
A: Manure type × soil	1	189	<0.0001
A: Manure type × char type	2	2.9	0.0560
A: Soil × char type	2	17.1	<0.0001
A: Manure type × soil × char type	2	10.3	<0.0001
κ*:* Intercept	1	26,224	<0.0001
κ*:* Manure type	1	46.4	<0.0001
κ*:* Soil	1	123	<0.0001
κ*:* Char type	2	3.3	0.0379

Table S2 Model parameters of the saturation curves' asymptote (*A*) and the exponential decay constant (κ) of modelled NH_3-N volatilization based on the fitted asymptotic model (means ± SE). Modeled **λ½** NH_3-N indicates the half-life of applied NH_4^+-N [**λ½** NH_3-N loss = ln(2) ÷ κ].

Treatment	Model parameter		R^2	**λ½ NH_3-N loss [h]**
	A [%applied NH_4^+-N]	κ [h^{-1}]		
PL	71.2 ± 1.5	0.07 ± 0.007	0.96	9.9 ± 1.8
PL+Hydrochar	69.5 ± 1.3	0.07 ± 0.006	0.97	9.9 ± 1.7
PL+Pyrochar	73.5 ± 1.6	0.08 ± 0.008	0.96	8.7 ± 2.2
CS	62.7 ± 1.2	0.05 ± 0.004	0.99	13.7 ± 2.1
CS+Hydrochar	52.7 ± 0.9	0.06 ± 0.004	0.99	11.6 ± 1.6
CS+Pyrochar	61.4 ± 1.1	0.06 ± 0.004	0.99	11.6 ± 1.8
PL+soil	40.5 ± 0.9	0.04 ± 0.003	0.98	17.3 ± 2.8
PL+Hydrochar+soil	41.1 ± 0.8	0.04 ± 0.003	0.99	17.3 ± 2.6
PL+Pyrochar+soil	40.7 ± 1.1	0.05 ± 0.005	0.97	13.9 ± 3.0
CS+soil	26.3 ± 0.4	0.03 ± 0.001	0.99	23.1 ± 1.4
CS+Hydrochar+soil	23.3 ± 0.4	0.04 ± 0.002	0.99	17.3 ± 2.1
CS+Pyrochar+soil	29.7 ± 0.9	0.04 ± 0.004	0.97	17.3 ± 3.8

10.3 Supplement for Chapter 8

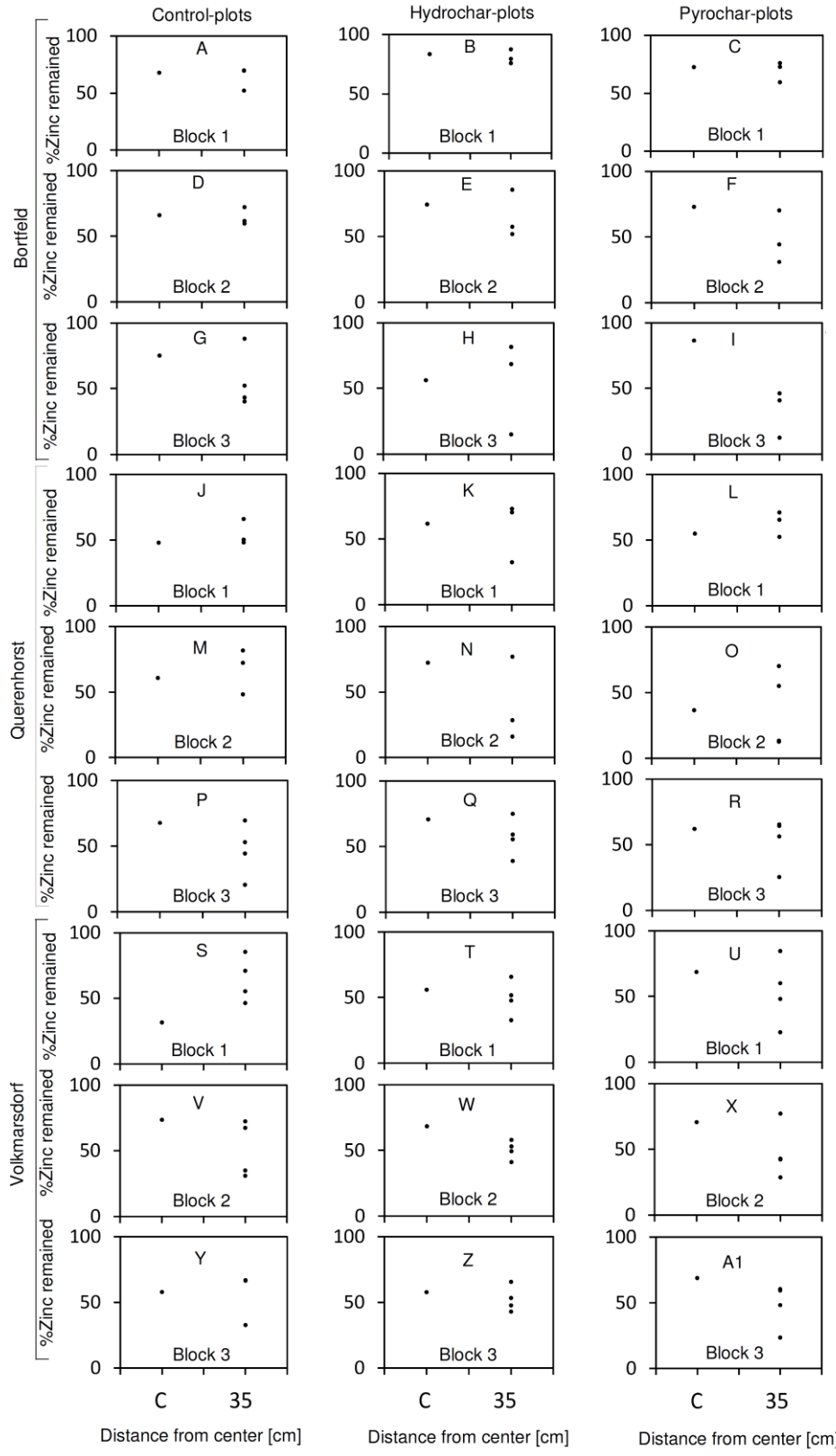

Figure A Distribution of %Zinc remained in soils from samples of each mini-plot at T_0. C indicates the center of each mini-plot.

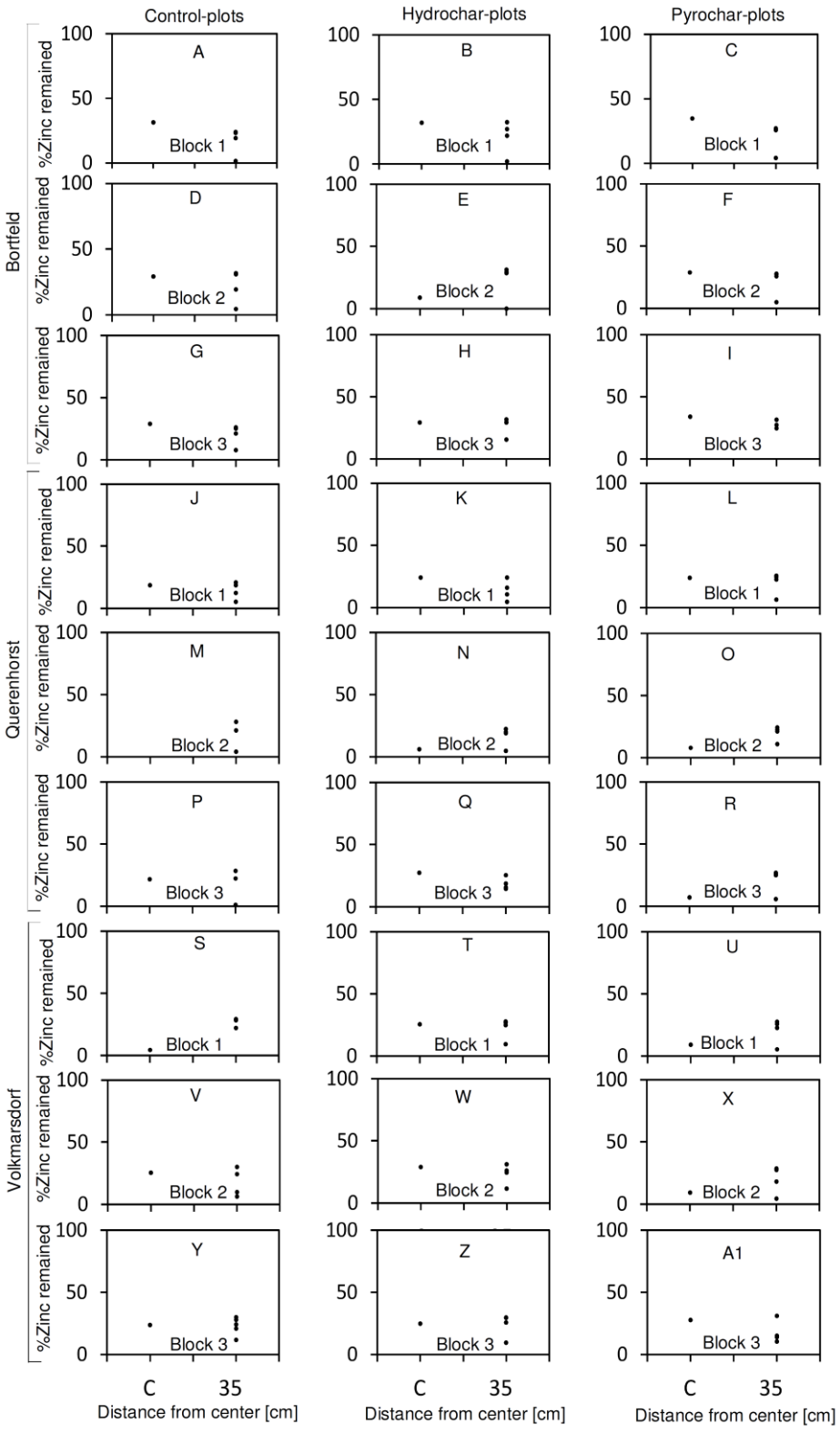

Figure B Distribution of %Zinc remained in soils from samples of each mini-plot at T_1. C indicates the center of each mini-plot.

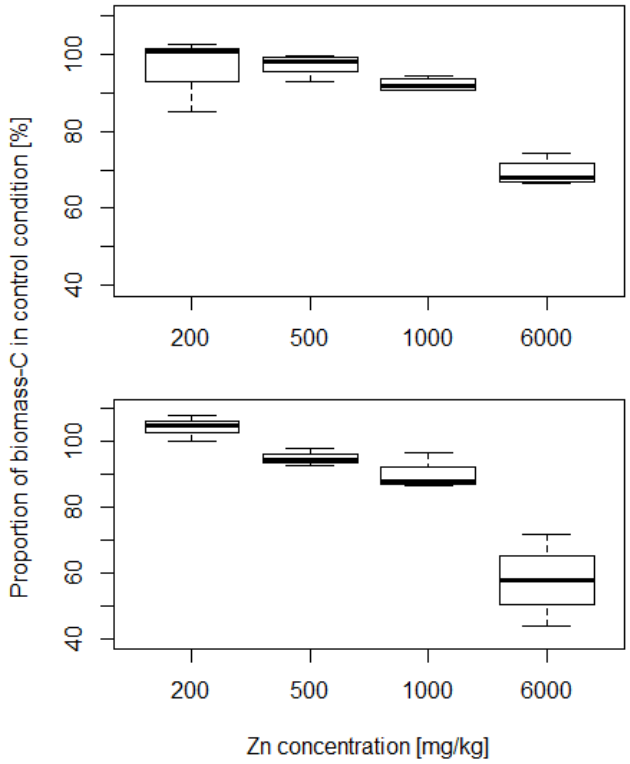

Figure C Effects of zinc on microbial biomass-C tested in two of the three soils that were used in the field experiment. All values indicate the percentage of microbial biomass relative to the control condition, where no Zn was added.

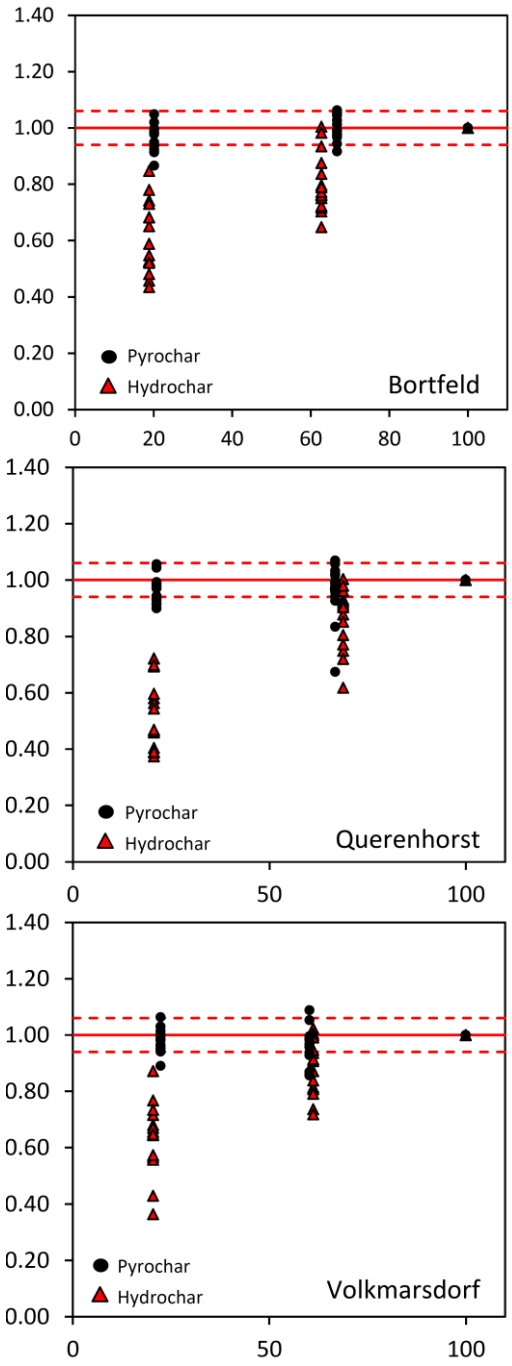

Figure D Ratio between %SOC to %Zinc (R_{ZnC}) vs. %Zinc remained in soil for all samples of the three experimental sites. Ratio = 1 (red solid line ± 95% confidence band) indicates decrease of chars in the same rate than the dilution of Zinc; Ratio < 1 indicates char mineralization; Ratio > 1 indicates unrealistic values, e.g., due to an increase of char in soils.

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13 WISSENSCHAFTLICHE BEITRÄGE

BEITRÄGE AUS DIESER DISSERTATION FÜR INTERNATIONALE/NATIONALE KONFERENZEN, SYMPOSIEN UND KOLLOQUIEN:

Gronwald, M., Vos, C., Don, A. and Helfrich, M. (2015): Biochar stability in agricultural soils during a 19-month field incubation in Northern Germany, using natural ^{13}C-abundance (**Vortrag**). Abschlusskonferenz "Regulation of soil organic matter andnutrient turnover in agriculture", 2015, Kassel-Witzenhausen.

Gronwald, M., Vos, C., Don, A. and Helfrich, M. (2015): Nutzung der natürlichen ^{13}C-Abundanz zur Untersuchung der Stabilität von Pflanzenkohlen aus *Miscanthus* in landwirtschaftlich genutzten Böden. Kommission 2, **Vortrag** V161. DBG Tagung 2015, München.

Gronwald, M., Don, A., Tiemeyer, B. and Helfrich, M. (2015): Loss of nutrient retention capacity of chars after seven-month in-situ field incubation **(Vortrag)**. Kolloquium des Department of Plant and Environmental Sciences der Universität Kopenhagen.

Gronwald, M., Don, A., Tiemeyer, B. and Helfrich, M. (2015): Loss of nutrient retention capacity of biochars after seven month in-situ field incubation **(Vortrag)**. International Biochar Symposium: Biochar Contribution to Sustainable Agriculture, 2015, Potsdam.

Gronwald, M., Don, A., Tiemeyer, B. and Helfrich, M. (2014): Biochar application to sandy and loamy soils for agricultural nutrient management. **Poster** B-162. EGU 2014, Wien. http://presentations.copernicus.org/EGU2014-6277_presentation.pdf

Gronwald, M., Don, A., Tiemeyer, B. and Helfrich, M. (2013): Biochar application to sandy soils: nutrient retention or leaching? Kommission 2, **Poster** 39. DBG Tagung 2013, Rostock.

BETREUTE ABSCHLUSSARBEITEN, DIE IM ZUSAMMENHANG MIT DEN DURCHGEFÜHRTEN VERSUCHEN STANDEN:

Vos, Cora (2014): Assessing the stability of different biochars in agricultural soils in Northern Germany, using a natural δ^{13}C label (Masterarbeit, Institut für Geographie, Universität Hildesheim).